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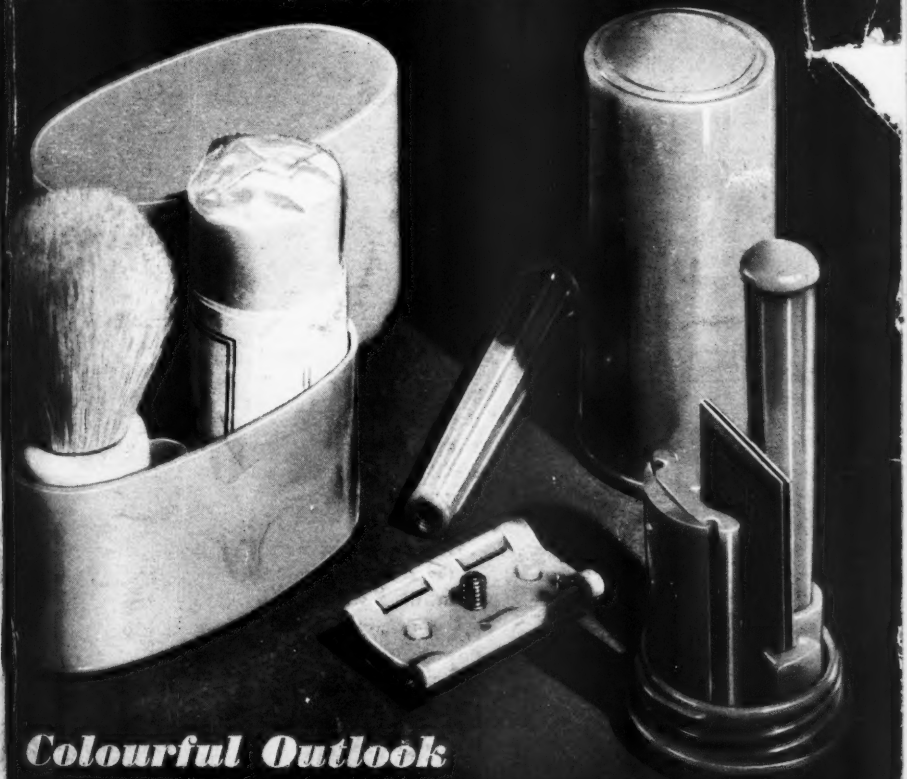

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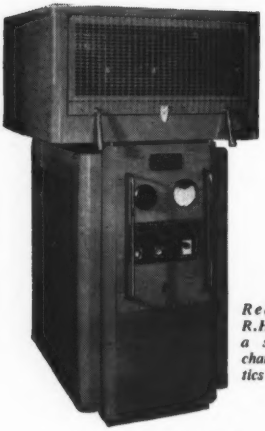

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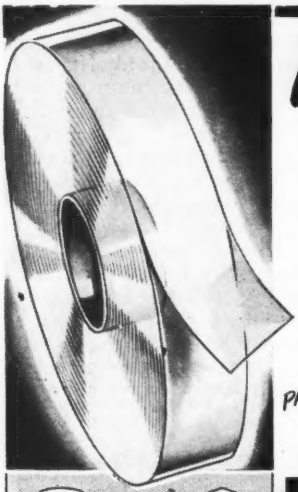

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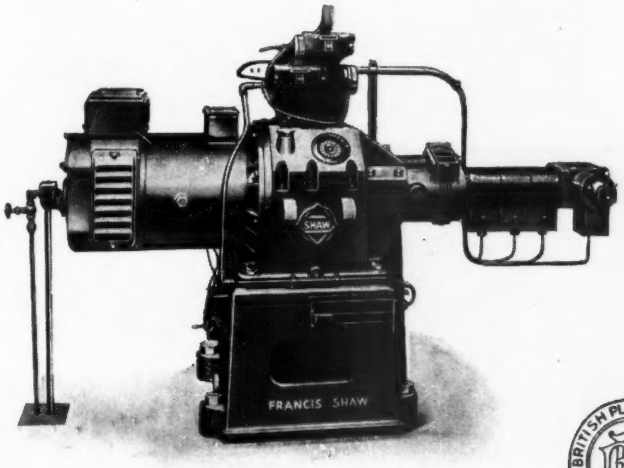

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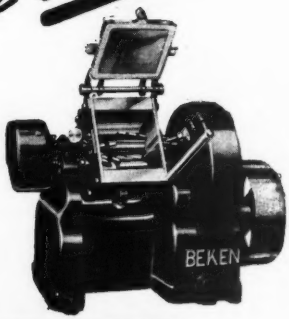

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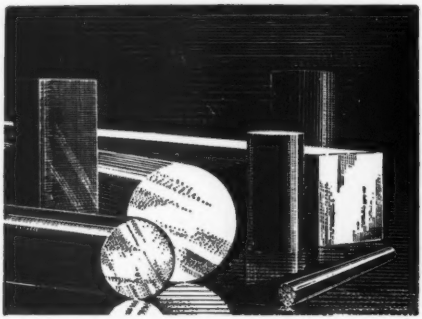

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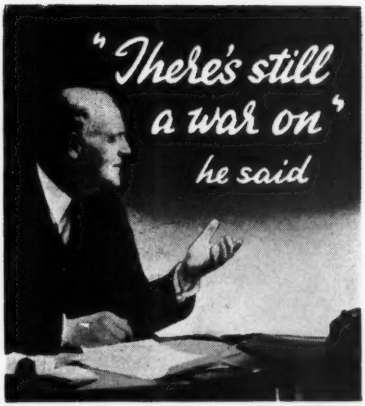

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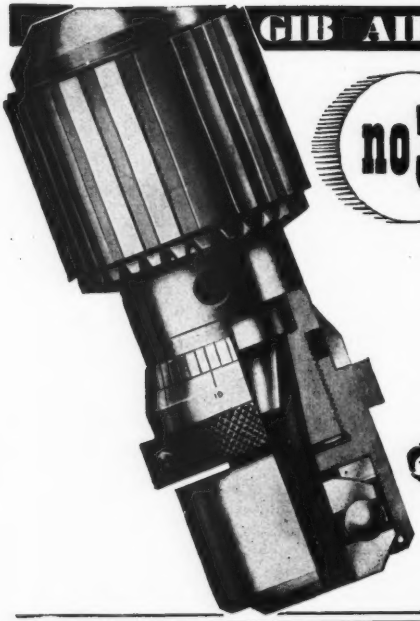

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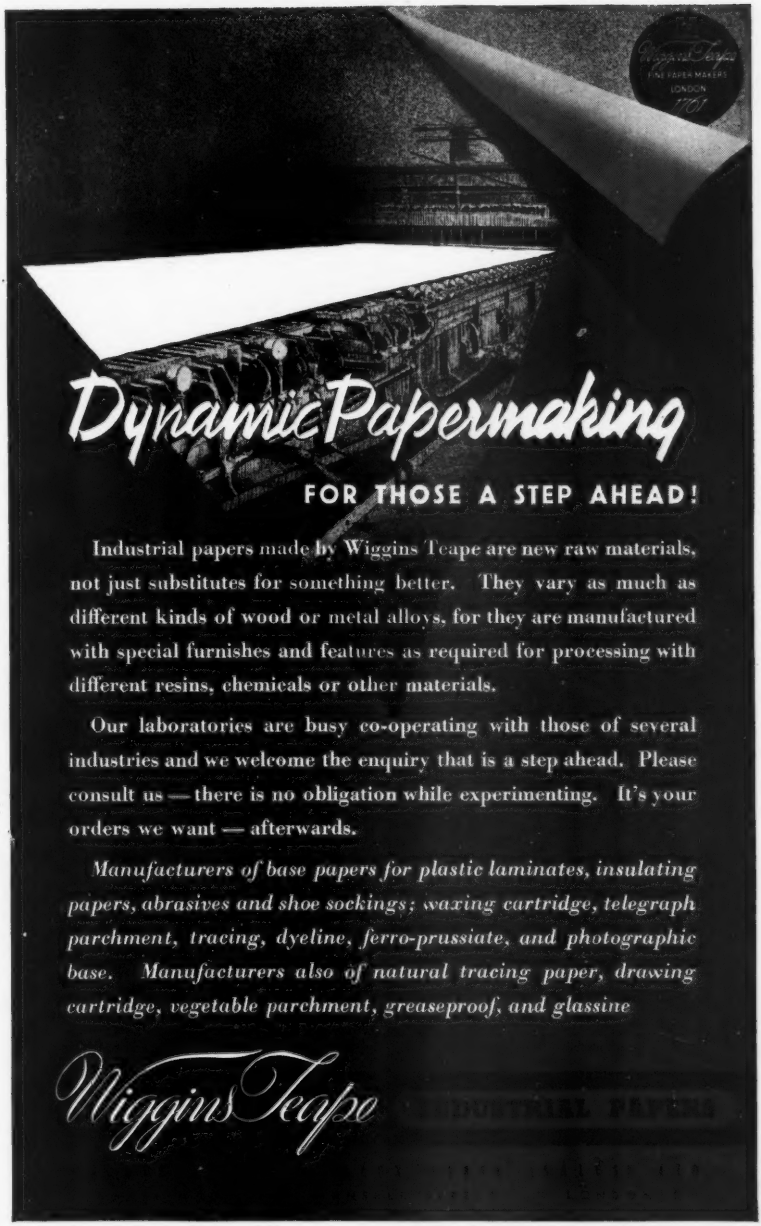
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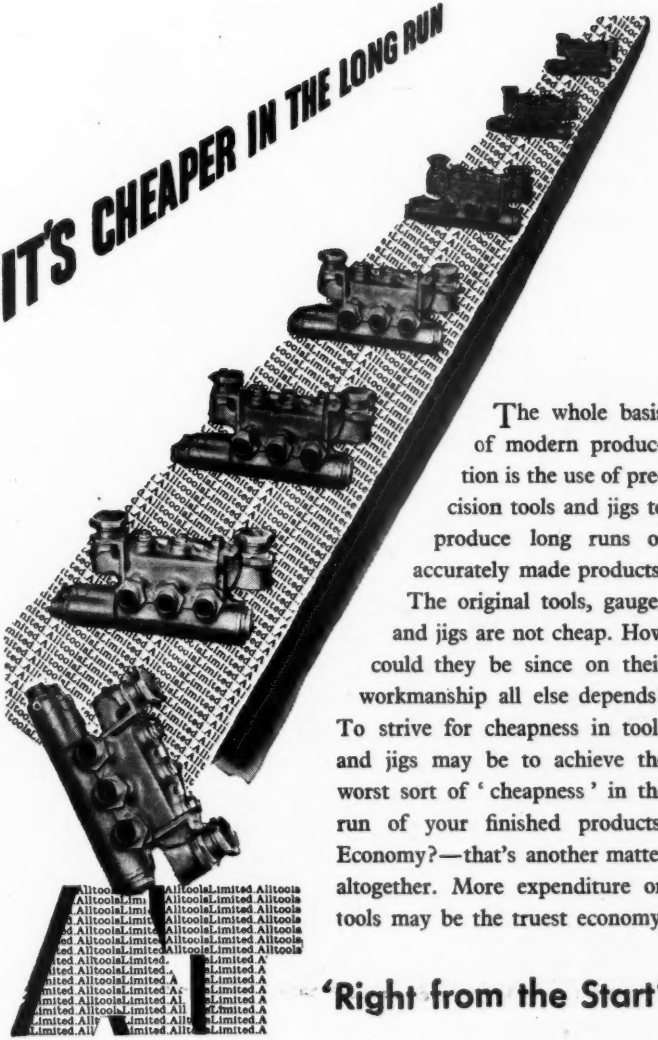

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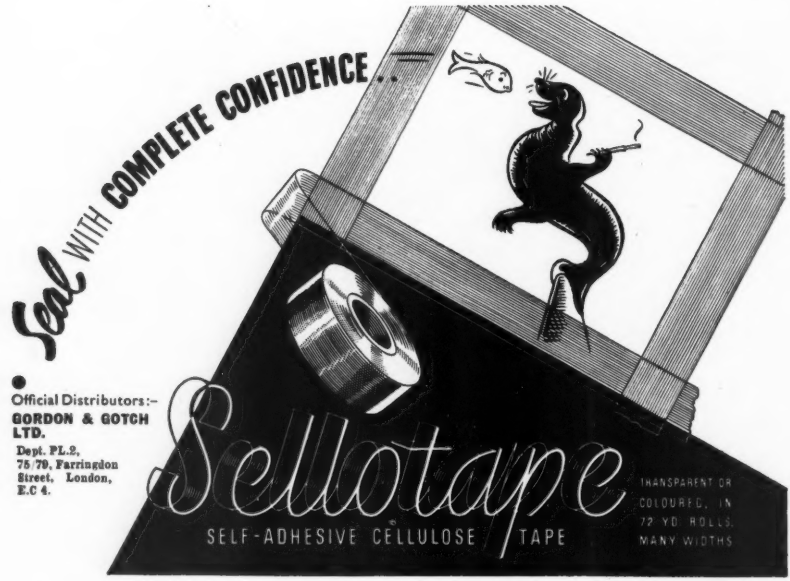
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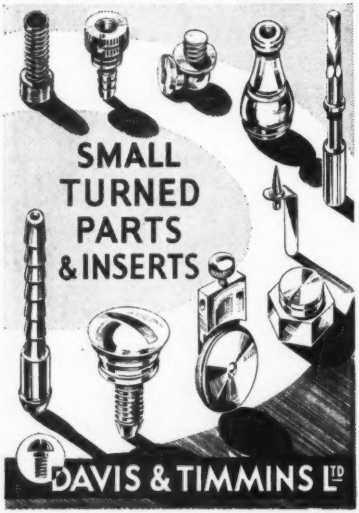

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Vol. X. No. 106 MARCH, 1946

Plastics

Dealing with the Manufacture, Uses and Potentialities of Plastic Materials

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NOTICES

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EDITORIALS

The Changing Industry

THE plastics industry has changed in a remarkable way in the last 10 or 20 years. This is especially true in its chemical aspect, which is in a state of continual kaleidoscopic mobility. This much we have seen and expect its continuation in the future as a result of concentrated world research.

There is, however, another change taking place before our very eyes, and one that has not yet been commented upon, although its importance is of the highest order. We refer to the change in economic orientation and the part the rubber industry is playing in it.

Twenty, or even ten, years ago, although all chemists and physicists knew that the common denominator of giant molecules linked rubber and plastics irrevocably together, and, indeed, knew that rubber is a plastic, the two industries were poles apart. There was often on the part of the older and larger group an attitude of complete indifference and more rarely of veiled hostility to the young "upstart." The latter, with impudent assurance, especially so far as electrical applications were concerned, adopted an air of "touch me if you can." We cannot blame the rubber manufacturers, for they have been tied for 120 years to a naturally produced commodity, and many were deeply involved economically in rubber plantations. Furthermore, the moulding of thermosetting resins was not their line of country. By 1936, however, they were regarding the enormously improved synthetic rubbers "Neoprene," "Thiokol," and "Buna" with considerable interest since these brought a degree of resistance to oil hitherto unknown. Of course, these compounds were not considered "plastics" by either side, but they nevertheless brought the two industries somewhat closer together.

It is not necessary to attempt to guess the course of events had war not broken out. It did break out, and the rubber industry went completely over to synthetics, which meant especially G.R.S., the copolymer of butadiene and styrene. From that point onwards it was obvious that all polymers must come under scientific examination by the rubber manufacturers, and soon polyvinyl chloride almost completely replaced rubber in many aspects for cable manufacture. By 1943 polythene was hailed as the answer to many a prayer, and this, too, was readily absorbed into the cable factory.

Now that war is over, the industry, with its vast experience of calendering rubber, has rapidly adopted p.v.c. for the production of sheet for a dozen purposes. The few well-known plastics manufacturers who originally specialized in this form of p.v.c. have since been joined by P. B. Cow, Veedip, Pirelli's, and others. We now hear that the latest recruits include Dunlops and the famous Silvertown company.

So far the interest appears to be in the polymers, and more especially the elastomers of this group, but, obviously, the quest will wander into the adhesive section and even into the phenolics and other groups. Already it is known that one of the best tackifiers for synthetic rubber is a phenolic resin.

How far this movement will go we will not hazard, although we know that one famous London rubber factory has contained a very complete moulding section for phenolics since the early years of the war.

Whether a complete integration is desirable, or even possible in a manufacturing sense, is beyond our province. In the realms of scientific thought, however, it is possible and desirable, and we have

already seen some useful aspects of it in the joint "plastics and rubber" scientific meetings. We are at last beginning to view the whole realm as a Large Molecule Industry and we shall reap benefit therefrom.

We have omitted to mention that in our very own field the rubber industry has stolen one march on us. During a recent visit to the Research Association of British Rubber Manufacturers, at Croydon, to renew old acquaintances, we saw in the fine library there the most complete index of polymer plastic materials and plastic processes we have yet seen in this country. New information is periodically circulated amongst the members of the Association.

At the risk of boring our readers with an old cliché, we must repeat that the dissemination of such information is the life's blood of an industry, and we are pleased that the British Plastics Federation has now had the foresight to take up the onerous task of providing it.

The true rubber factories in this country have not yet manufactured plastics, but the American companies have long taken a very lively interest in the matter. This refers more especially to companies like the B. F. Goodrich Corporation. We were most interested to hear recently that the Distillers Company are combining with the B. F. Goodrich Chemical Co., of Cleveland, Ohio, to form British Geon, Ltd., and to produce polyvinyl chloride and various copolymers in this group.

In Gorgeous Technicolor

LAST month we wandered into a Leicester Square Cinema where "The Last Chance" and a documentary film entitled "Plastics" were being shown; although we did not blue six bob to see the latter especially, it is that we wish to discuss.

It was made, we understand, by the British Council, a Government-fostered body which hitherto has spent some of your money and ours to explain to foreigners something of British life, mainly in the form of art and letters. It has now taken unto itself the task of showing something of British industry to Britons in Britain. The film "Plastics" is part of that task.

We wish we could say it was a good film for it must have cost a lot of money and it may prove of value to have a central organization to act as ambassador and compère to our goods. Besides, we want as much high-quality publicity as we can get.

Technicolorfully speaking, there were some bright spots, but as for the story, it seemed that it was chosen mainly because it could be treated in Technicolor and not for its own value; moreover, it was not only unbalanced but totally inadequate.

To an audience composed of workers in the plastics industry, the film would in part have proved a good one. The production of phenolic resins was portrayed very satisfactorily as was the moulding of them to produce radio cabinets and coloured telephone receivers; so too was the fabrication of laminated material.

On the whole, however, according to the British Council, plastics appear to consist mainly of casein for making knitting needles and of celluloid, materials that only one in a hundred individuals in the plastics industry has ever seen in the raw state. Both, in their way, are important, especially to the fancy-goods trade, but if so much stress is laid on them as being the backbone of our industry we shall not get very far. They do not form the backbone, but are merely a couple of ribs.

We hazard a guess that the audience came away thinking that plastics were lovely and wonderful and that they are nearly all made from skimmed-milk, the only recognizable raw material noun that struck their ears. We are sure they made nothing of "feenoll." We are not surprised that housewives are writing to the Sunday papers protesting that their children need more milk and can do with less plastics.

We hazard a second guess that none of the audience knew why plastics are used

and had become important in the past 20 years. Not a word was there to indicate why they had so fundamentally transformed the electrical industry and how they had made electricity safer. The intelligence of the British Council only saw the "appeal" of a green or red telephone set and the lovely brunette who held it to her shell-like ear. And never a word to explain why plastics have entered the engineering, textile, furniture, aircraft, shipping and chemical industries, replacing metals or wood or rubber or stone when and where plastics prove themselves better in use.

It cannot be overwhelmingly difficult to describe in pictorial form the formation of large organic molecules and that they can be hard or soft and elastic or soft and inelastic, or tough, and why most of them are resistant to electricity, water, acid, alkali and oil. If this were then "tied-up" with your beautiful brunette and her telephone, or a plastic table top, there would be some coherence and use in the film.

We come to the conclusion that Walt Disney would have made a much better job of it with his latest technique.

Down with Resinoids!

DURING the same film, while describing the phenolic resins, the commentator uttered the mysterious word "resinoid." He said it lovingly, as some love to say new and complicated words their hearers have never previously heard. It is a sonorous-sounding one, but what intellectual snobbism to bring it in when so few know that the Greek suffix "oid" merely means "resembling"! We bet the commentator himself had never heard it before. Certainly in this three-syllable novelty the audience saw no relation to "resin" and battled through a fog of incomprehension.

We have always disliked this new word, the illegitimate union between a Latin noun and a Greek suffix, but admit its use in a technical journal. Even so, we look forward to its ultimate disappearance, especially because natural resins no longer appear in the plastics industry itself and are, indeed, being used less and less in paint and lacquer manufacture. Synthetic resins have for most purposes become the superior resins and if we stick to the word "resinoid," some genius in the natural-resin industry, in order to say how closely his products resemble the synthetic variety, may yet announce them as "resinoidoids."

Pretty Picture

READERS will, we are sure, forgive us for the trivial photograph we have reproduced on page 125. Truth to tell, we "go in for" growing things during odd moments and thought the snowdrops worth while photographing. There is a plastic angle to it, for the "pot" is a "Perspex" dome we obtained from Dr. John Sisson, of I.C.I., under entirely false pretences. The "earth" is polystyrene made by crushing some electrical injection mouldings of Distrene, the growth of the bulbs being promoted by the use of hydroponics.

"Plastics—Scientific and Technological"

The second edition of H. R. Fleck's book has now been published. Its appearance so soon after the first edition was made is a good indication of its worth. Indeed, we believe it to be by far the best of its type that has yet appeared, especially in the comprehensive manner in which the whole picture of the plastics industry is drawn, and in the way theoretical concepts and production in practice have been described.

This expansiveness, if we may so call it, is shown throughout, but a specially excellent example is seen in the way in which he describes the use of synthetic resins in the paint and varnish industry, a subject which most writers on plastics technology avoid like the plague. Obviously, however, Mr. Fleck is an expert in many branches of our industry, and is, therefore, able to draw the chain of analogy round many related ones.

The new edition shows signs of being added to advantageously. We note the inclusion of a special section on silicon plastics, which brings the book right up to date. Published for Temple Press Ltd. by The English Universities Press, Ltd. Price 30s. net.

Electrical Plastics in U.S.A. (Continued)

Dichlorostyrenes and Their Polymers

By E. E. HALLS

FURTHER information on the progress in America made with the chlorination of styrene compounds is given by J. C. Michalek and C. C. Clark, of the Mathieson Alkali Works (Inc.), N.Y., in an article entitled "Dichlorostyrenes and Their Polymers," which appeared in "Chemical and Engineering News," September 25, 1944, p. 1559. This is abstracted below.

The impetus was given to the research by the heat resistance shortcomings of polystyrene and its compounds, the shape and dimensional failure of polystyrene below 100 degrees C. and the serious loss of strength at elevated temperatures of the co-polymerized styrene-butadiene compound (GR-S or Buna-S synthetic rubber). Additions to these products, when they have given improvement in the direction of heat resistance, have caused deterioration with respect to other valuable properties. The Mathieson solution to the problem was reached by modifying the styrene nucleus itself to dichlorostyrene, which, when polymerized, is said to combine the electrical insulating qualities of polystyrene with excellent heat resistance. Further, when co-polymerized with butadiene, a rubber is obtained, which is superior to Buna S.

The nuclear substituted dichlorostyrenes were prepared from the corresponding dichlorobenzaldehydes by the formation of carbinols through the Grignard reaction, followed by dehydration in the vapour phase over activated alumina. The following properties are recorded:—

Dichlorostyrene isomer	N_D^{25}	Boiling point °C	Density 25/4
2,6	1.5724	59 at 2 mm.	1.280
3,5	1.5745	53.5 at 1 mm.	1.237
2,5	1.5788	74 at 3 mm.	1.245
2,4	1.5812	69 at 2.5 mm.	1.246
2,3	1.5780	61 at 1 mm.	1.264
3,4	1.5840	76 at 3 mm.	1.243

Generally, these isomers have a surprisingly pleasant odour, particularly the 3,4 isomer, of which the smell resembles that of geraniums.

The monomeric dichlorostyrenes are very active in the direction towards polymerization. High purity samples have polymerized virtually to completion in 3 to 4 hrs. at a temperature of 60 to 70 degrees C. It is, however, possible to work with cross-sections of less than ½ in. and keep the reaction temperature below that which would be injurious to the polymer.

The hydrocarbon styrene itself normally requires from 8-14 hrs. at 130 degrees C. for polymerization, and at the end of this time it still contains from 1 to 3 per cent. of monomeric styrene. In contrast with this, the great activity of dichlorostyrene takes the polymerization to a degree in which the monomer does not exceed about 0.1 per cent.

Impurities affect the polymerization reaction. Generally, they are detrimental, and break the chain reaction of polymerization. Some impurities are not chain breakers. Thus sulphur in the monomer as sulphur dioxide in small amounts seems to aid the growth of long chains, whereas in the form of hydrogen sulphide it has the reverse effect. This is shown graphically in Fig. 1, which gives the relation between temperature of polymerization and the molecular weight of the polymer for dichlorostyrene, and for dichlorostyrene with sulphur dioxide addition and with hydrogen sulphide present.

With 0.1 per cent. of p.-tertiary-butyl-alcohol catechol present polymerization proceeds but at a reduced rate.

The polymers from each of the isomeric dichlorostyrenes are all hard, transparent, colourless substances that resemble polystyrene in chemical resist-

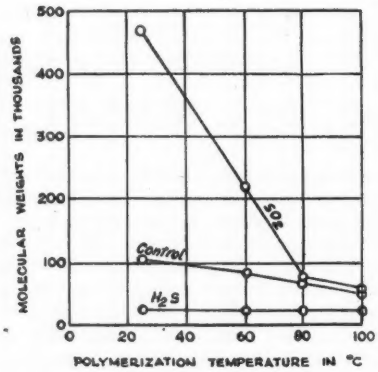


Fig. 1.—Effect of SO_2 and H_2S on molecular weight of dichlorostyrene polymer.

ance, solubility and general appearance. With the exception of the 3,4 polydichlorostyrene, the polymers are all soluble in aromatic hydrocarbons, chlorinated solvents, some esters and higher ketones. They are not soluble in aliphatic hydrocarbons, lower alcohols, ethers and glycols. Some solvents, such as acetone and higher alcohols, swell but do not dissolve the dichlorostyrene polymers.

The solubility of the exception noted above, the 3,4 polymer, is interesting. Although it is a linear polymer, it is insoluble in toluene, with which only slight swelling occurs at the boiling point. It is insoluble in carbon tetrachloride and in mixtures of carbon tetrachloride and toluene. It is slowly but completely soluble in methyl ethyl ketone.

The dichlorostyrenes can be polymerized in mass, or in true emulsion, the latter giving a latex-like product before coagulation, and very finely powdered resin after coagulation.

The monomers may be dispersed in water using gelatine, talc, bentonite, polyvinyl alcohol or other conventional stabilizers, and polymerized as beads or pearls, and perfectly clear spheroids can be obtained.

It is also noted (Automotive and Aviation Ind. 89, 26-27, 66-80 (1943)) that the trichlorostyrenes, properly prepared, are surprisingly active monomers, having boiling points of 82 to 84 degrees C. at 2 mm. and a refractive index (D, 25 degrees C.) of 1.5943. They polymerize very readily, and the resultant resins have A.S.T.M. distortion temperatures of 120 degrees C. and higher, and they can be co-polymerized to rubber-like products.

The Mathieson polydichlorostyrene plastic has a distortion temperature of 240 to 265 degrees F., which is higher than for any plastic that combines excellent electrical characteristics with good strength, machineability and mouldability. To prevent impairing the high-temperature properties of the product, high purity in the monomer and careful control of polymerization conditions are necessary.

Mathieson plastic is self-extinguishing to ASTM D-635-41T. When held in a flame, it undergoes pyrolysis and the products of pyrolysis burn. When the flame is removed, the pyrolysis stops and there is no further burning. The combustion products are carbon dioxide, water, soot and hydrochloric acid.

The Mathieson plastic retains its hardness to a remarkable degree at 200 degrees

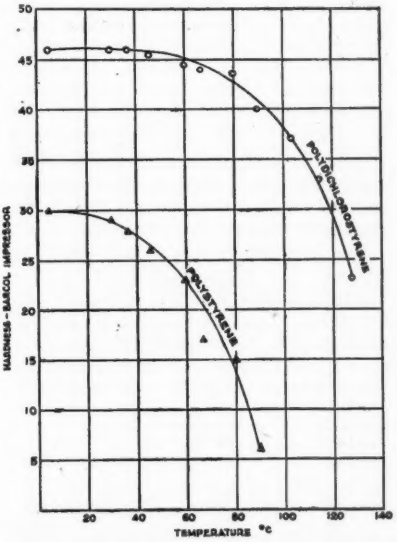


Fig. 2.—Hardness at various temperatures for injection moulded samples.

Table 1.—Properties of Mathieson Plastic*

Characteristic	Mathieson plastic	Polystrene*	Cellulose acetobutyrate*
Moulding qualities	Good	Excellent	Excellent
Compression moulding temp., °F.	350 to 425	275 to 375	260 to 360
Compression moulding pressure, lb./sq. in.	2,000 to 5,000	1,000 to 10,000	500 to 5,000
Injection moulding temp., °F.	475 to 525	325 to 500	340 to 420
Injection moulding pressure, lb./sq. in.	10,000 to 30,000	10,000 to 30,000	8,000 to 30,000
Specific gravity	1.39 to 1.40	1.054 to 1.070	1.15 to 1.23
Refractive index, N_D	1.62 to 1.64	1.59	1.47 to 1.49
Flammability, in./min. (ASTM-D-635-41T)	Self-exting.	0.75 to 1.50	2.50 to self-exting.
Tensile strength, lb./sq. in.	4,600 to 7,460	3,000 to 8,500	2,500 to 6,700
Modulus of elasticity, lb./sq. in. $\times 10^5$	5.0 to 7.0	1.7 to 4.7	0.6 to 2.0
Flexural strength, lb./sq. in.	14,000 to 19,000	4,800 to 19,000	2,100 to 12,700
Impact strength, ft. lb./in. of notch (ASTM-D256-41T)	1.0 to 1.5	0.26 to 0.4	0.5 to 7.5
Hardness, Rockwell	>M100	M55 to M95	M23 to M72
Distortion under heat, °F.	240 to 265	165 to 190	117 to 214
Dielectric strength, volts/mil	370	500 to 700	250 to 400
Dielectric constant	2.55 to 2.65	2.5 to 2.7	3.5 to 6.4
Power factor (per cent.)	<0.1	0.01 to 0.08	1.0 to 6.0
Water absorption, 24 hrs. (per cent.)	0.02	0.04 to 0.06	1.6 to 2.1
Effect of weak acids	None	None	Slight
Effect of strong acids	None	None	Decomposes
Effect of weak alkalies	None	None	Slight
Effect of strong alkalies	None	None	Decomposes
Effect of organic solvents	Soluble in aromatic and chlorinated solvents	Soluble in aromatic and chlorinated solvents	Soluble in ketones and esters
Effect on metal inserts	Inert	Inert	Inert
Clarity	Transparent	Transparent	Transparent
Colour possibilities	Unlimited	Unlimited	Unlimited

*From "Technical Data on Plastic Materials," by Plastic Materials Manufacturers' Association.

F. and above. This is clearly shown in Fig. 2, which gives hardness values measured by means of a Barcol impressor in an oven at various temperatures. Polystyrene and polydichlorostyrene are both included.

A detailed comparison of properties for the Mathieson polydichlorostyrene, for polystyrene and for cellulose acetate-butyrate are given in Table 1. The Rockwell hardness value of M.100 approaches that of the thermosetting resins. Tensile and flexural strengths are higher than normally for polystyrene, and impact strength substantially higher. It does not become brittle at naturally occurring low temperatures.

The Mathieson plastic is more compatible with conventional plasticizers than is polystyrene itself. This makes a valuable range of cements and pressure-sensitive adhesives possible.

In electrical applications, one is always nervous of the possibility of chlorine or hydrochloric acid being freed from chlorinated plastics under service conditions of humidity, heat, light, etc. It is to be expected that, with the chlorine substituted in the benzene ring, and not in the side chain, good stability will be attained. It is claimed that with the Mathieson plastic no stabilizer is required, and that no hydrochloric acid is liberated even in moulding, or at any temperature short of actual pyrolysis.

Water absorption for the Mathieson plastic is lower at all temperatures than it is for polystyrene. This is shown for mouldings in Fig. 3.

Regarding chemical resistance, Mathieson plastic tested by ASTM methods is unaffected by hydrochloric acid, nitric acid, sulphuric acid, ammonium hydroxide, sodium hydroxide, dilute and concentrated, at room temperatures. The absorption in sulphuric acid of S.G.1.26 at 90 degrees C. was found to be less than 0.1 per cent. by weight in 48 hrs. and no measurable hydrochloric acid was liberated during the test. It is unaffected by methyl and lower alcohols, aliphatic hydrocarbons, glycols and vegetable oils. It is soluble in aromatic hydrocarbons, chlorinated hydrocarbons, some esters and ethers, methyl ethyl ketone and some higher ketones.

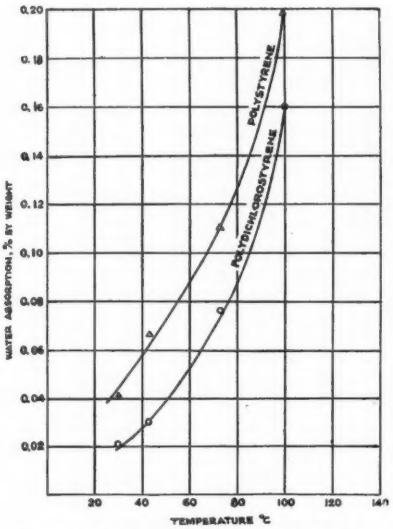


Fig. 3. — Water absorption (24 hours' immersion) at varying temperatures for injection mouldings.

The material may be moulded by the usual methods except in so far as its high distortion temperature and melting point render some modifications necessary to the injection moulding and extruding technique. Sprues, runners and gates need to be as large as is consistent with the cavities, and it is advisable to operate the mould at 140-160 degrees C. to avoid premature setting in these cross-sections. Otherwise, chilled portions may prevent the complete filling of the mould. Mouldings much hotter than is normal with thermoplastics can be removed from the moulds and handled without risk of distortion. For some shapes, the moulding cycle can be longer than is the case with polystyrene. If the moulding machine has been used for most other thermoplastics, such as nylon, polystyrene, cellulose acetate and acetobutyrate, it can often be used immediately with Mathieson plastic without difficulty other than moderate sticking until the previous material has been completely flushed out of the machine cylinder.

Compression moulding may be used, but it is not generally recommended because of the extremely long cycle. Shapes can be produced by extrusion processes, but proper cooling and annealing are necessary to obtain stability.

Co-polymerization with other unsaturated substances is readily achieved by mass or emulsion methods. True co-polymers have been formed with the following substances:—Styrene, alpha methyl styrene, methyl acrylate, methyl methacrylate, acrylonitrile, vinyl acetate, dimethyl furane, piperylene, quinine, 2-methyl pentadiene, dimethyl butadiene, butadiene, maleic anhydride, isoprene, cyclopentadiene, indene, chloromaleic anhydride.

Many of the co-polymers are rubber-like. Compounded in formulæ of the GR-S type, they show improved properties as follows:—

(a) Oil resistance.
(b) Tensile strength.
(c) Elongation.
(d) Tear resistance.
(e) Modulus at 300 per cent.

These better properties show not only at normal temperatures, but also at 212 degrees F. The values after ageing for 48 hrs. at 212 degrees F. are not reduced to nearly the same extent as they are with GR-S. The Goodrich, De Mattia and St. Joseph flexometers, as well as road tests, show excellent resistance to flex-cracking. The material is also easier to mill than is GR-S.

Table 2.—Compounding and Properties of Mathieson Rubber

Mathieson rubber	100 parts by weight			
Bardol	5			
Zinc Oxide	5			
W-6 Black	50			
Sulphur	2			
Captax	1.5			
Curing temperature	280° F.			
Chlorine in crude rubber, %	8.8	12.5	16.2	23.2
Curing time, minutes	70	70	70	80
Tensile, psi	2,530	3,490	3,960	2,400
Elongation, %	490	735	745	560
Modulus at 300% elongation	1,230	690	840	—
Durometer hardness (Shore)	65	61	60	73
Set, %	13	28	31	38

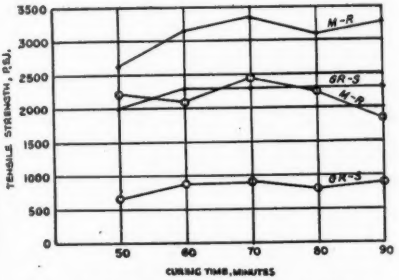


Fig. 4.—Tensile strength of unaged Mathieson rubber (18.7% chlorine). Solid circles represent values obtained when samples tested at room temperature, the open circles when tested at 212°F.

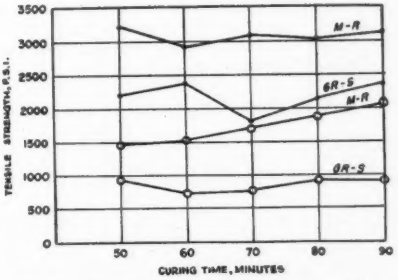


Fig. 5.—Tensile strength of Mathieson rubber (18.7% chlorine). Aged 24 hours at 212°F. Solid circles represent tests made at room temperature, open circles at 212°F.

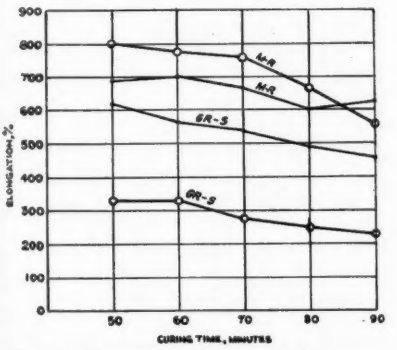


Fig. 6.—Elongation of unaged Mathieson rubber (18.7% chlorine). Solid circles represent tests at room temperature, open circles at 212°F.

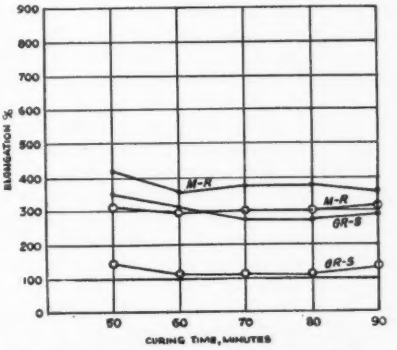


Fig. 7.—Elongation of Mathieson rubber (18.7% chlorine), aged 24 hours at 212°F. Solid circles represent tests at room temperature, open circles at 212°F.

Compared with natural rubber, the Mathieson copolymer rubber plastic excels on oil resistance, hot tensile strength, resistance to heat ageing and water absorption.

Table 2 gives a tread stock, compounding conditions and properties. In this application, the amount of dichlorostyrene has a controlling influence on quality, and a chlorine content of 12-16 per cent., equivalent to 30-40 per cent. of dichlorostyrene, is found to be best. Superior heat resistance of rubbers from the lower end of this range is shown by Figs. 9 and 10.

Regarding the low-temperature flexibilities of these rubbers, that compounded to the conditions given in Table 2 is more satisfactory at the lower end of the 12-16 per cent. chlorine range. With 14 per cent. chlorine, the rubber product was slightly hard at −50 degrees C. and broke at −65 degrees C. Smoked sheet compounded by the same formula was hard at −50 degrees C. and did not break at −60 degrees C.

The milling characteristics of the Mathieson rubber plastic are excellent, the material handling very much like smoked sheet. As one example, Mathieson rubber broke down in 2 mins. sufficiently to begin adding the black, as

Table 3.—Compounding Formula

Rubber	100 parts by weight
E.P. Channel Black	45
Zinc oxide	5
Sulphur	1.7
Santocure	1.2
Stearic acid	2.5
B.L.E.	2.0
Pine tar	2.5
Bardol	2.5

against 5 mins. for GR-S. In another, breakdown was 2-3 mins., accelerator added in 4 mins., black in 11 mins., softener in 14 mins., zinc oxide in 15 mins., and sulphur in 16 mins.; the stock was cut off in 18 mins., and then refined for 3 mins. The temperature of the stock was about 120 degrees F.

The superior properties of Mathieson rubber (18.7 per cent. chlorine content) compounded by the GR-S formula, and cured at 280 degrees F. over those for GR-S, are demonstrated by the curves in Figs. 4-8 inclusive. Each shows test values for material prepared with various curing times, the test being made both before and after ageing for 24 hours at 212 degrees F. and being taken at room temperature and at 212 degrees F. Tensile strength, elongation and modulus at 300 per cent. are included.

Figs. 9 and 10 similarly refer to a Mathieson rubber containing a lower chlorine content of 12.9 per cent. and to a GR-S compounded to the formula given in Table 3. The curing temperature was 287 degrees F. and the stearic acid was omitted from the GR-S material.

It will be seen that the tensile strength of this copolymer rubber is 4,350 lb./sq. in. at room temperature, and 4,000 lb./sq. in. after ageing for 48 hours at 212 degrees F. The hardness value of the 18.7 per cent. chlorine rubber was 88 after ageing, and of the 12.9 per cent. chlorine rubber 70, which is a more desirable value. A comprehensive summary of hardnesses for various cures is given, before and after ageing, for 24 hours at

Table 4.—Shore Hardness of Mathieson Rubber Compounded by GR-S Formula

Chlorine in Mathieson rubber 18.7 per cent.; tested at room temperature

Curing time, minutes	Unaged		Aged 24 hours at 212° F.	
	Mathieson rubber	GR-S	Mathieson rubber	GR-S
50	64	57	84	69
60	64	59	87	70
70	66	60	88	72
80	68	61	88	73
90	69	61	88	73

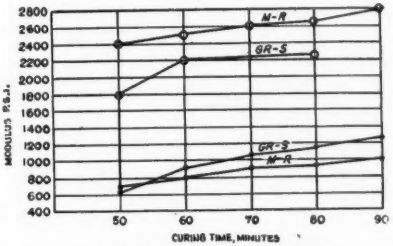


Fig. 8.—Modulus at 300% elongation of Mathieson rubber (18.7% chlorine). The top two curves relate to material aged for 24 hours at 212°F. The lower curves refer to unaged material.

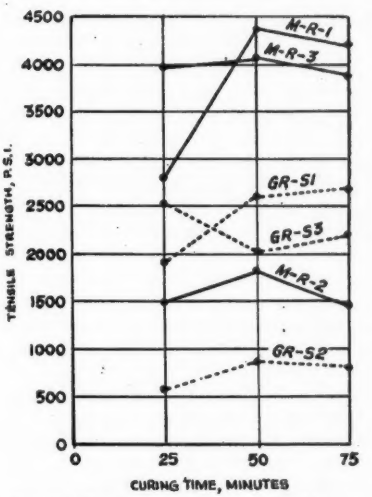


Fig. 9.—Tensile strength of Mathieson rubber (12.9% chlorine). Data are from tests made at room temperature and the curves numbered 1 represent unaged samples, 2 represent the samples tested at at 212°F. and 3 represent samples aged for 48 hours at 212°F.

Table 5.—Winklemann Tear Test on Mathieson Rubber Compounded by GR-Formula.
Chlorine in Mathieson rubber 18.7 per cent. : curing temperature 280° F.

Curing time. minutes	Unaged				Aged 24 hrs. at 212° F.			
	Tested at room temp.		Test at 212° F.		Tested at room temp.		Test at 212° F.	
	Mathieson rubber	GR-S	Mathieson rubber	GR-S	Mathieson rubber	GR-S	Mathieson rubber	GR-S
50	315	175	265	120	215	165	255	210
60	330	275	240	175	245	175	280	235
70	300	230	220	185	320	195	270	195
80	310	245	250	170	310	165	270	215
90	265	230	265	185	255	140	270	160

212 degrees F., in Table 4, with GR-S included for comparison.

The outstandingly better tear characteristics of Mathieson rubber are shown by the Winklemann Tear Test results given against those for GR-S in Table 5. This data embraces a range of cure time, tests at room temperature and at 212 degrees F., and before and after ageing for 24 hours at 212 degrees F.

The Mathieson rubber compounded to the information given in Table 3 was also checked for resistance to flex-cracking on the St. Joseph, Goodrich and De Mattia flexometers, and resistance shown to be excellent. On the De Mattia machine, GR-S failed at 54,000 flexings, and after ageing at 26,000 flexings, whereas the Mathieson rubber had still not failed at 100,000 flexings. Again, in a heat build-up test involving 30 mins. of flexing, GR-S rubber rose in temperature to 324 degrees F. when it blew out, while the Mathieson rubber did not fail and rose only to 228 degrees F.

Table 6 gives analytical data on two batches of Mathieson rubber of the types discussed and represented by the above mechanical test results.

Table 6

Chlorine (Parr bomb), % ..	12.9	18.7
Dichlorostyrene, %	31.5	45.6
Iodine value (Wijs)	277	217
Toluene solubility by Soxhlet extraction, %	90	79.4
Molecular weight on soluble portion (Oxtwald viscosimeter) ..	190,000	148,000

Table 7

Chlorine content of Mathieson rubber, %	15.5	20	30
Specific permeability—			
Hydrogen	9.2	6.2	1.9
Helium	6.1	5.0	2.1
Carbon dioxide	18.7	7.4	—

Table 7 gives specific permeability values for Mathieson rubbers of various chlorine contents, the figures being ml. of gas passed through per cm. of area per sq. cm. of thickness per minute, multiplied by one million. The values are very low, and become progressively lower as the chlorine content rises. It is suggested that the material is of interest as a possible coating for balloon cloth.

Electrical characteristics taken on a sheet of compounded Mathieson rubber 6 by 6 by 0.070 ins., and containing clay, zinc oxide, EP channel black, paraffin, stearic acid, antioxidant, sulphur and accelerator, were as under:—

Specific inductive capacity .. 5.0
Power factor at 1,000 cycles 4.5

Water absorption was measured on crude sheets of Mathieson rubber 5 by 2.5 by 0.08 ins., immersion being for 20 hours at 70 degrees C. The values in comparison with those for other rubbers are given in Table 8, the figures being mgm. per sq. in. of surface (neglecting edges). The Mathieson rubber is superior to crepe and far superior to GR-S, Hycar OR and smoked sheet.

Fig. 11 shows the oil resistance of

Table 8

Sample	Absorption
Mathieson rubber	2.2
GR-S	25
Smoked sheet	18
Special crepe	3
Hycar OR	33

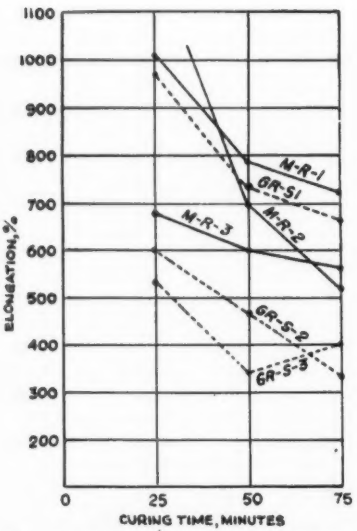


Fig. 10.—Elongation of Mathieson rubber (12.9% chlorine). In this figure, curves 1, 2 and 3 have the same description as in Fig. 9.

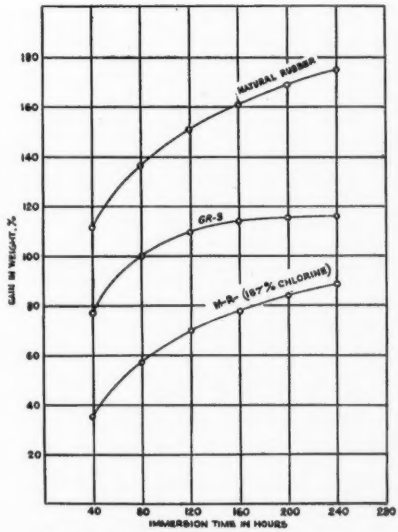


Fig. 11.—Weight gain of tire stocks immersed in light Circo oil at 55°C.

Mathieson rubber, gaining weight with time of immersion in light oil at 70 degrees C. being recorded. It is superior to both GR-S and natural rubber; but it is noted that it is not so good as neoprene, Hycar OR and Thiokol. These are not shown in the figure.

The hardness of Mathieson rubber can not only be controlled by the amount of sulphur incorporated, as is the case with hard rubber prepared from natural rubber, but also by adjusting the amount of dichlorostyrene in the crude. Tough, dense and hard products can be produced for resistance to acids and alkalis at moderate temperatures.

The foregoing information is the result of the co-operative efforts of the Mathieson Alkali Works Inc., the General Tyre and Rubber Co., Whyte Manufacturing Co., Phelps-Dodge Copper Products and National Bureau of Standards.

It is probably true to say that the polydichlorostyrenes are practically unknown and not available in this country. This is surprising in view of the extensive work carried out in America, not only on these polymers themselves, but on the copolymers to give rubber-like bodies. There is certainly a field for them, and the thermal resistance of the polydichlorostyrenes superior to that of other thermoplastics, with good electrical properties, claims their consideration in radio communications equipments. It may be that research is required towards an improvement in power factor, but this is not necessarily too difficult. The copolymers, in the electrical field, have many possibilities, particularly as cable coverings, in which field the polyvinyl chlorides, extensively employed to-day, are not necessarily the final word, particularly when thermal stability is entailed. Flexible film material, superior to anything known in this country, with respect to thermal stability and flexibility, is still sought for small insulation and for moisture-proof and gas-proof membranes. The possibility of the polydichlorostyrenes in film form, or as copolymers, or as coating on silk or paper is promising. Their availability in this country is looked to with more than interest.

SALUTE TO SPRING
AND PLASTICS

By M. D. C.

Photograph by H. Reid (Temple Press Photographic Staff)

The Microscopic Examination of Plastic Materials

VI.—Mouldings: (a) Fillers (Wood Flour)—contd.

By J. H. WREDDEN, F.R.M.S.
(Chief Chemist, Igranic Electric Co., Ltd.)

IN the last article we dealt with the histological elements of a woody plant from the point of view of their usefulness as a filling material for moulding powders. We examined chiefly those elements which occur as strengthening members, and saw how they varied in structure, some obviously being stronger than others. We also saw, briefly, how these tissues are located in the general structure of the plant.

It is now proposed to take this examination of the structure of wood a step farther, because, as has been pointed out, if we are going to use wood flour as a filling medium in the most efficient manner possible, then obviously we have got to know something of the nature of the wood from which the flour is produced. The best way of obtaining this is by a study of its histology. It should therefore be borne in mind that whereas these notes may at first sight appear irrelevant to the subject under discussion, they are in fact very necessary to the proper understanding of the best methods of using the material.

Therefore, let us proceed with the examination of the stem structure. It was pointed out in the previous article that in some cases the cambium cut off a continuous ring of xylem tissue instead of forming bundles, as described diagrammatically. These bundles are conspicuous in those plants which regenerate the stem every year, such as the sunflower. This is clearly shown in Fig. 63, which is a photomicrograph of a transverse section of a sunflower plant at a magnification of 80 diameters. Here we see all the tissues discussed, making up the entire assembly, as it were, shown at "A." This is collectively known as a vascular bundle and includes the massive bast fibres shown at "B," the area occupied by the sieve tubes at "S," both of which are outside the cambium layer shown at "C." This will be seen to traverse the width of the vascular bundles and the space between them. Immediately inside the cambial ring we have the bunch of trachieds and vessels collectively known as xylem (X) in which the large diameter tubes are the vessels, while the smaller ones are the trachieds. From an examination of this vascular bundle it will be seen that well over 50 per cent. of the cross-sectional area is made up of the strong fibrous elements in the bast and xylem tissue

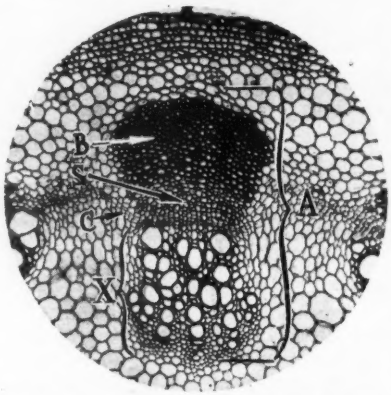


Fig. 63.—Transverse section of sunflower showing a typical vascular stem. Mag. 80 diams.

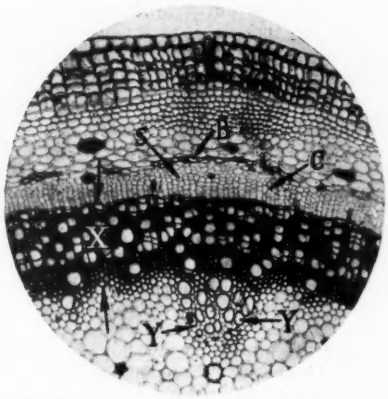


Fig. 64.—Transverse section of elder stem. Mag. 80 diams.

Fig. 65.—Transverse section of lime tree, first year. Mag. 80 diams.

(B and X). The whole of the xylem portion will be seen to be embedded in a mass of living parenchyma cells which go to make up the pith. Thus we see that even the lowly annuals possess elements which may be of great use as a filling material and as such are worthy of being remembered.

Now let us examine another type of woody structure as found in the elder. A transverse section of an elder stem at 80 diameters is shown in Fig. 64. This shows the structure of the xylem (X) to take the form of a continuous ring which is laid down in the latter part of the year. Those xylem elements which are formed in the early part of the year are seen to take the form of a bundle shown at "Y," where it will be noticed that the percentage of large vessels (V) is higher than in the ring portion of the xylem. The cambium layer may be seen at "C," while the sieve tubes "S" are seen to be arranged in a ring similar to that of the xylem. The bast fibres, on the other hand, are few in number and irregularly spaced, these are shown at "B." From this we may conclude that as the only tissues of interest to us are the xylem and the bast, this particular wood is only rich in xylem and therefore would not be particularly suitable as a filling material, also the large quantity of pith would complicate matters somewhat.

Thus we see, in progressing up the scale in size of the woody plant, how we find the xylem percentage is increasing, for it is obvious that the xylem content of the section in Fig. 64 is higher than in Fig. 63, so now let us take another step up this scale, look at the primary structure of a tree, taking for our example the lime. The first year's growth is shown in transverse section in Fig. 65, again at a magnification of 80 diameters. Here we see that the central parenchymatous portion is very much reduced, only a small portion of it is visible in the photograph at "A." The xylem, however, occupies the greater proportion of the cross-section, extending for the distance "B"; here again we have the continuous ring formation, although in this case the tissue is more compact. A noteworthy feature of this section is in the narrow medullary rays, one of which is illustrated at "M." The cambium layer is seen at "C" and a phloem bundle at "P." The phloem in general is seen to be formed into definite bundles and not to be a continuous layer, it is very rich in bast fibres which possess highly lignified walls, so much so, that the cell cavity is almost entirely obliterated. The section is further

interesting, as it shows the birth of an annular ring, that is to say we see the commencement of a new xylem ring starting the second year of growth. This is shown at the point " D " where the large spring vessels laid down by the cambium in the spring of the second year are clearly seen, against the smaller trachieds of the autumn wood formed at the end of the first year.

So we see a further increase in the xylem content when we come to examine the highest type in the scale; in fact, it should be remembered that in all trees the greatest proportion of the volume of the trunk is occupied by xylem. The phloem occurring in the thin extra cambial layer generally referred to as the bark is the living portion which is responsible for the nourishment of the cambium and hence the growth of the tree.

As the phloem occupies such a small proportion of the whole and the only tissue element of much use to us is the bast fibre, we may leave this portion of the tree for the time being and focus our attention on the xylem or woody portion, from which wood flour, as we know it, is produced to-day. There are several points which are worth bearing in mind when considering the xylem in relation to the manufacture of wood flour required as a filling material for moulding powders; chief of these is perhaps the development of the dead " heartwood."

As the trunk of the tree increases in diameter, so it becomes more difficult for atmospheric oxygen to penetrate to the innermost rings, thus suffocating the living tissue, in the form of the parenchymatous cells, which are found in the medullary rays. These cells, as has been pointed out, virtually form the flesh of the plant and carry large quantities of starchy and sugary material in storage, as it were, and while they are alive the xylem is actively functioning as " sapwood " and transporting fluids about the body of the tree; however, as soon as the oxygen supply is interfered with the parenchyma cells start living on their stored material and when the contents of the cells are exhausted, they die and, at the same time, the xylem ceases to function as a fluid transporting medium; instead it dries up and the medullary rays do likewise, the whole forming a closely knit structure which now functions as a true internal skeleton of mature " heart " wood.

Thus the woody portion of a tree may be divided into two distinct areas, the dead and dry heartwood in the centre which is surrounded by the moist living sap wood; this latter usually occupies a more or less narrow band immediately against the cambium, whose depth naturally depends on the diameter of the trunk and the age of the tree.

The significance of the foregoing remarks lies in the assumption that, for our wood flour we want the cellulose and lignin (ignoring for the time being the various forms in which these two materials are available), without other substances being present. Therefore, it will be seen that as the mature or " heartwood " is the only portion where we obtain this required degree of purity, the flour should be produced from heartwood only. Thus one could say that in buying wood flour, the best policy would be to specify " heartwood " or more usually mature wood as against seasoned wood; this latter means that the wood has been artificially dried by a seasoning process, and the ambiguity of the term will be appreciated when it is realized that it is quite possible to cut a tree down before it is ready. In other words, before there is sufficient heart wood to produce any real quantity of well matured wood. This means that a larger portion of the trunk is sapwood and whereas cutting down the tree and drying it will remove the moisture, and kill the parenchymatous tissue, this element will still contain the starchy and sugary cell contents, hence the wood itself is weakened and for our purpose these storage materials are the very last thing we would desire in a finished moulding, particularly from the electrical standpoint. Mature wood can only be produced by the natural death of the parenchyma and the subsequent absorption of the cell contents; it cannot be produced artificially. So that as a

result of this preliminary excursion into the histology of wood, we have suggested to us one method by which an improvement in the quality of wood flour may be generally effected, for the rule applies to all woods. This, of course, assumes that the usual practice in the industry is to obtain wood flour, as such, without reference to any particular specified qualities. It would, no doubt, be quite interesting to know how many powder manufacturers pay attention to this basic point when purchasing wood flour.

So far, we have dealt with only one type of woody plant, actually there are two distinct types classified with relation to their seed structure. The first, with which we have already dealt, is known as dicotyledonous and is characterized by massive secondary growth and reticular venation in the leaves. The second type, known as monocotyledonous, is characterized by the grasses and similar types of plant with parallel ventation. A study of the structure of the stem shows it to be greatly different from that of the dicotyledonous plants; a typical "monocot" stem is shown in transverse section in Fig. 66. This is a photomicrograph of a section of the stem of the maize plant (zea mais) at a magnification of 45 diameters. The different type of structure is clearly shown and consists of numerous vascular bundles (A) distributed in an uneven manner throughout the stem. It will be noticed that they are more numerous towards the periphery of the stem, the centre of which is occupied by parenchymatous tissue (B) in which the bundles are embedded.

The structure of these vascular bundles is interesting inasmuch as they consist of the three main tissues, viz.: xylem (C) containing one or two large vessels and numerous trachieds; adjacent to the xylem mass is the phloem (D) containing sieve tubes (E) surrounded by a mass of heavily thickened bast fibres (F). The point of main interest, however, lies in the absence of a cambium, this obviously precluding any development of secondary wood, hence the restricted growth of this type of plant. However, the "monocots" should not be ignored as a source of material for filling powders, as in a number of cases the bast and xylem regions would appear excellent prospects for this purpose; for example, some of the varieties of cane are very rich in fibrous tissue.

Having made a brief histological survey of wood in general and seen the more relevant characteristics of the two types, i.e., "Dicotyledon" and "Mono-

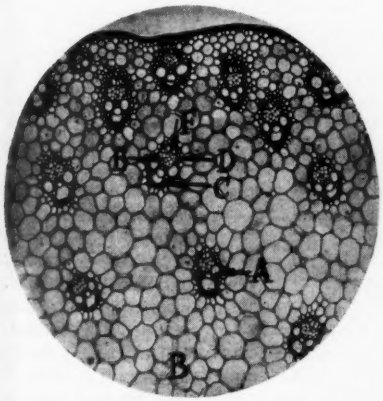


Fig. 66.—Transverse section of stem of maize. Mag. 45 diams.

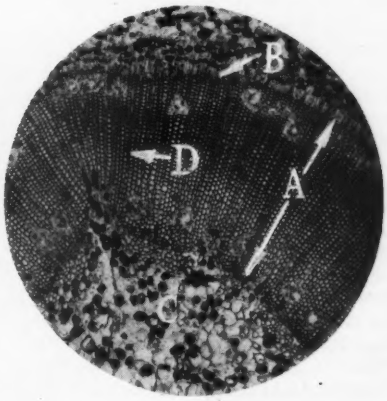


Fig. 67.—Transverse section of Pinus Silvestris first year. Mag. 45 diams.

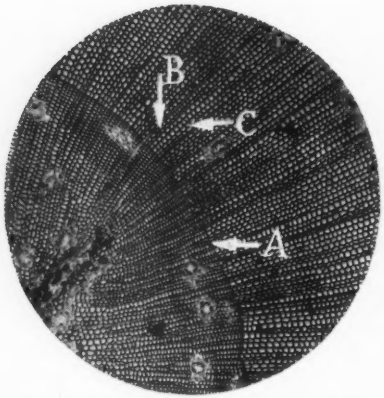


Fig. 68.—Transverse section of stem (Pinus Silvestris, 2nd year growth). Mag. 50 diams.

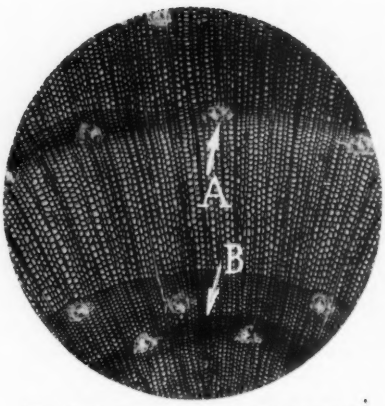


Fig. 69.—Transverse section of 3-year-old stem (Pinus Silvestris). Mag. 50 diams.

cotyledon," let us examine a specific case applicable to the main study.

According to Dahl* the great majority of wood flour used in the plastics industry is obtained from coniferous wood, i.e., from trees of the cone-bearing variety, such as pines and spruces, etc. These are generally termed softwoods, while the deciduous woods, such as oak, ash and the like, are more usually classed as hardwoods. Therefore, let us examine the structure of the softwoods in relation to their use as filling powders. We may take as a typical example the Scots fir (Pinus Silvestris), which shows the structure so characteristic of this species in general. Thus, in Fig. 67 we see a transverse section of the stem of this plant, after the first year of growth, at a magnification of 45 diameters. The xylem ring is clearly seen extending for the distance (A) bounded on the outside by the cambium (B) and on the inside by the parenchymatous core (C). All woods of this type appear to possess xylem composed entirely of pitted tracheids which we shall examine in detail subsequently. However, it is worth noting that the xylem vessels are generally small in diameter and densely packed, being liberally interspersed with fine medullary rays such as that shown at D. It will also be noticed how the diameter of the xylem elements becomes considerably reduced towards the outer boundary of the woody ring; the reason for this has been previously explained.

On examining the structure of this species after the second year of growth, we see the development of the second ring of xylem tissues, as shown in Fig. 68. The original location of the cambium is quite clearly seen at the sharp line of demarkation (A), where the autumn wood of the first year ceases and the spring wood of the second year commences. The difference in the diameter of the elements is very marked; we also see how the primary medullary rays follow straight through with the second-year wood, as shown at (B), while the secondary medullary rays commence with the beginning of the second year, such as at (C). The characteristic reduction in diameter of the tracheids towards the end of the year will also be noticed in this second-year wood. This gradual diminution in size is, of course, an automatic process and occurs in each yearly growth.

This change in size is again evident in Fig. 69, which shows the stem of a three-year-old fir (only the xylem portion is shown) at the same magnification, also

* Dahl. "Wood Flour."

the manner in which the primary medullary rays continue through the third-year wood will be seen. At the same time, it will be noticed that the secondary rays are developed in the second-year wood and continue through the third year; at the same time, further secondary rays will be seen to have been generated in the third-year wood. This process of continuation of rays developed in each succeeding year takes place throughout the entire structure of the tree, from which it will be seen that a compact mass of xylem is produced with elements taking up directions at right angles to one another.

There are other structures which appear in this and the preceding illustrations, one of which is shown at (A), Fig. 69. These are resin ducts in cross-section and consist of a tube lined with living patenchyma of a specialized kind, whose function is to secrete the resin which fills the ducts. These ducts are numerous, and it should be remembered that when the xylem has died and become heartwood the resin still remains in the ducts, and thus, if precautions are not taken for the removal of the resin, it will be present in wood flour made from this wood and will, in all probability, have a deleterious effect on a moulding powder and final moulding in which it is incorporated.

It is interesting to note that climatic changes during the development of the tree are capable of causing modifications to the xylem, thus at the point (B), Fig 69, we have a sudden development of a band of small tracheids during the first year of growth. This was, in all probability, brought about by poor weather conditions over an extended period, which, when cleared, resulted in the normal process of development taking place.

Apart from this, the rate of growth appears to vary with the climate in which the tree is grown, so that in temperate climates the tree flourishes and grows rapidly, forming wide rings which, according to Henderson,* may be as few as three or four to the inch. On the other hand, the same author quotes 20 to 40 rings to the inch in wood grown in rigorous Baltic climate, and more numerous still if grown in districts farther North, such as Archangel. Thus it will be appreciated that between these two extremes lies a compromise of structure and mechanical strength, and as we require the maximum mechanical strength, we must obviously give preference to a wood somewhere in between these two extremes, assuming that we can only use these coniferous woods.

After having examined the general structure, in cross-section, of our example of the conifers (Primus Silvestris), let us look at the xylem portion in somewhat greater detail. It should be borne in mind that there are three methods of sectioning a tree trunk, the first being the transverse section, which we have already examined, the second is a longitudinal section in the direction of a diameter of the stem. This shows the vessels and other elements in longitudinal section in their correct relation to one another. The third method is known as a tangential section and consists of a section taken in the direction of a chord of the transverse section, thus one would obtain an end-on view, as it were, of the medullary rays.

Suppose we now

Fig. 70.—Longitudinal section of conifer (Pinus Silvestris). Mag. 150 diams.

* Henderson. "Timber" Crossby Lockwood.

examine a longitudinal section, such as that shown in Fig. 70. This photomicrograph is at a magnification of 150 diameters and shows the wood to be composed of tracheids having a pitted thickening of lignin. This type of pit is characteristic of the coniferous woods and constitutes a valuable aid to identification, as this type of wood is composed entirely of these tracheids; there do not appear to be any vessels or elements thickened in any manner other than that shown. Likewise the thickening is all of the same type, i.e., possessing bordered pits, as seen at "A." The tracheids themselves are relatively short in comparison with those found in the deciduous woods, one such being shown at (B). Thus it will be seen that the entire xylem of the conifers is built up of these tiny units, which are not very highly lignified and are, therefore, not particularly strong individually, but when taken en masse the structure does possess appreciable mechanical strength, apparently by virtue of its close-knit nature. In all probability a good deal of the mechanical strength owes its existence to the presence of similar tracheid chains in the medullary rays; a portion of one such ray is seen in the illustration with its tracheids, one of which is shown at "C." Thus we have a system of tracheids which, incidentally, are the strongest elements in the wood, progressing at right-angles to each other, and the reason for the strength of the wood becomes evident.

Fig. 71.—Tangential section of conifer. Mag. 150 diams.

A further point of interest in this particular section lies in the parenchyma cells of the medullary ray shown; these cells obviously still retain their starchy contents, as shown at "D." Therefore, one could conclude that the wood from which the section was made was still living when cut, and as such would not be a great deal of use as a filling powder owing to the large amounts of starchy material which would be present, for we have seen that the medullary rays are almost as numerous as the layers of tracheids. In this instance there would be a considerable proportion of starchy material in the powder; this point is raised to illustrate the views expressed earlier, on the desirability of using only fully matured wood.

Now let us examine a tangential section of this conifer. This shows an appearance similar to that in Fig. 71, at a magnification of 150 diameters. We see the tracheids "A," which apparently do not possess any pits; this is due to the fact that the coniferous tracheids are more or less, quadrilateral in cross-section and only possess pits on the opposite faces whose direction is parallel to a radius of the cross-section of the stem.

Passing in between the tracheids and pushing them to one side are the medullary rays. These are seen in cross-section as at "B" and are quite numerous. In the centre of the illustration is seen a large medullary ray containing a resin duct "C."

Thus we see that the softwood from which the majority of wood flour fillers are produced is composed of masses of pitted tracheids of varying cross-section and approximately 1/32-in. long. The pitting takes the form of large bordered pits sparsely distributed about the tracheid which is not very highly lignified, in consequence of which the element itself

would not appear to be very strong (mechanically). The general structure, however, is such that large masses of these tracheids are interspersed with considerable numbers of medullary rays, which also carry two or more tracheids of a similar nature, thus we get a tightly interwoven structure of lignified tracheids, which, presumably, accounts for the strength of the wood in general.

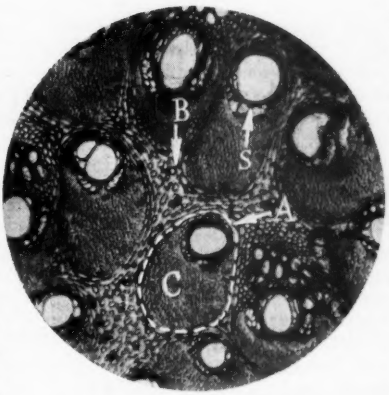


Fig. 72.—Transverse section of Ballata cane. Mag. 150 diams.

Freely distributed throughout the structure in both directions are the resin ducts, the presence of which would appear to be undesirable owing to the necessity for removing the resin for the purpose of powder making.

From these remarks it would appear that to make the most efficient use of this type of wood for filling purposes it would have to be broken down in such a manner as to leave the tracheid elements whole so that their full mechanical strength may be developed; we shall, however, discuss this in greater detail subsequently.

The wood also would seem to require very careful selection if the inclusion of considerable quantities of sugary and protein matter is to be avoided. This would obviously be one of the first considerations in cases where the flour is intended to produce mouldings requiring good electrical properties.

The presence of natural resin in the moulding would appear to be somewhat undesirable, due to the possibility of it making the moulding brittle. With regard to its effect on the electrical properties, this is a debatable point, as on the one hand natural resin in the form of colophonium is a good insulator, but on the other hand its acidic properties might cause it to be suspect, due to the possibility of the occurrence of free acid in the moulding. Therefore, it would appear to be a wise precaution to take steps for the removal of natural resin, or, better still, use a non-resinous wood, which latter, as we shall see, should hold promise of greater mechanical strength.

It is now proposed to leave this examination of the coniferous for the time being and proceed to deal in a similar manner with the deciduous types, but before examining this latter it would perhaps be as well to have a look at a "monocot" wood, as it is the author's opinion that these plants, i.e., the canes, have been neglected as a source of supply of filling materials. Thus, in Fig. 72, we see a transverse section of the stem of a Ballata cane at 150 diameters, which shows a typical "monocot" structure, but on comparing it with the stem of the maize plant, it will be seen that the vascular bundles (A) are very much more tightly packed; the basic parenchyma (B) occupies only a relatively small percentage of the whole.

The vascular bundles themselves are quite massive structures, very rich in bast fibre tissue, which we have seen is highly lignified and possesses high mechanical strength; such an area is shown at "C"; the bundles possess only one large vessel with few sieve tubes "S" lying adjacent to them. Altogether, the whole structure would appear to offer considerable possibilities for use as a source of filling powder; in fact, a planimetric analysis of the section illustrated shows that at least 25 per cent. of the tissue is composed of bast fibres, therefore, it is suggested that this type of material might be worth investigating.

(To be continued)

World's Industry Employs Plastics

GENERAL ENGINEERING

Friction weld joining of plastics developed in U.S.A. promises to simplify numerous engineering assembly problems, more especially in general engineering construction in which plastic components are embodied with others of metal. The friction welding process is applicable only to thermoplastics and at present can be used only in joining compositions of identical types. On a laboratory scale, however, it is made with some success for the joining of plastic components to wood and to metals. The process demands the use of a small high-speed drill press, lathe, or smaller machine. One plastic component mounted in a suitable fixture is rotated at high speed and brought into light contact with the surface to which it is to be welded. After a few seconds contact "flow" occurs at the abraiding faces; at this point rotation is stopped and the surfaces are brought tightly together using the hand feed of the drill or lathe. ("Materials and Methods," 1945/**22**/1728.) **Standards on plastics** form the subject matter of a recent publication by the American Society for Testing Materials. Containing the most recently developed specifications for methods of testing plastics, the third edition of this handbook presents in a convenient form more than 100 specifications and tests involved in the production of these, with representatives of both producers and consumers (in U.S.A.) of the materials under discussion. Committee D-20 of plastics was responsible for the descriptive nomenclature. In addition to this the book contains 33 methods of testing, 23 specifications, and five recommended practices contributed by the same committee. In the field of electrical insulation will be found 24 specifications and numerous testing methods, recommended practices and definitions. Committee D-9 is responsible for this part of the publication. Further details may be obtained from "Machine Design," 1946/**18**/159, from which journal the publication itself may be obtained (price $2.75). **"Plaspreg," a plaster of paris base impregnated with liquid thermosetting resins** subjected subsequently to curing by heat, forms the subject of a paper by Delmonte in "Machine Design," 1946/**18**/174. It is shown that the resin saturated plaster body retains, after completion of treatment, the characteristic crystalline structural network of the natural plaster, although in appearance and feel it resembles dies for forming sheet metal under the hydraulic press, duplicating dies and patterns for the Keller machine and contour shapes for working acrylic plastics. Obviously, it may also be used for general patterns of industrial and decorative value. The use of a furone resin is recommended in so far as it is of low cost, is easy to fabricate and, used in conjunction with plaster, improves the physical, chemical and thermal properties of this latter material. Most important, age shrinking of the plaster is eliminated. Prior to impregnation, parts must be thoroughly dried and should, as far as possible, be produced in very carefully prepared plaster. The impregnation process means some delay occurring before the plasterboard can be used and it should be borne in mind that although the resulting product is stronger than the unimpregnated material it, nevertheless, is still relatively

brittle. **Valve of Neoprene in engineering design** is discussed by Kosler in "Product Engineering," 1946/**17**/61. It is shown that the basic properties of Neoprene correspond closely with those of natural rubber and the material is said to compare favourably with the latter as regards the following features:—Resistance to petroleum and oils, chemicals, sunlight, dry heat, and flame contact, specific gravity, and tensile strength are considered at full length. During the war the bulk of the Neoprene produced was used for gasmasks, lifebelts, life rafts, protective coatings and, of course, for a multitude of aircraft purposes. Neoprene 1-32-in. thick is used as a substitute for grease on stretch presses in aircraft plant. **Swiss Standards Association** has issued several specifications dealing with plastics. Specification VSM 77011 deals with the nomenclature and recommends abbreviated designations for about 32 plastics; French and German terms are covered, for example T.St. stands for polystyrene foils; T stands for thermoplastics; "fo" stands for foils. Standard VSM 77012 deals with tolerances and it is pointed out that moulded parts require larger limits than is customary in the specification for metal parts. Tolerances are subdivided into separate groups, those conditioned by the mould and those independent of manufacture. Further tolerances for wall thickness and for bending deflection and other deformation are given. A special specification VSM 77021 deals with laminated and non-laminated thermosetting moulding materials and includes statements on mechanical, electrical and chemical properties. VSM 77022 deals with paper, textile and wood laminates, and also covers mechanical properties. It is pointed out in all standards that the specifications presented do not conform to corresponding standards published by the German Standards Committees. **S.P.I. Standard (U.S.A.) for tolerances on moulded plastic parts are presented in "Product Engineering,"** 1946/**17**/172. The standard presents data collected on the moulding tolerances and dimensional stability and moulded thermoplastic and thermosetting resins, excluding the laminates. Tolerances are presented in three sections—fine, standard and coarse. The materials dealt with include wood flour filled phenolics, cotton flock filled phenolics, rag filled phenolics, tire cord paper filled phenolics, short fibre asbestos filled phenolics, long fibre asbestos filled phenolics, asbestos and wood flour filled phenolics, mica filled phenolics and unfilled phenolic resins. In addition, urea moulding compounds with alpha cellulose fillers and all qualities for electrical purposes are also covered. Melamine moulding compounds, both with cellulose and asbestos fillers and with rag fillers are further dealt with. Finally, cellulose acetate of medium flow acetate butyrate of medium flow, ethyl cellulose medium flow, general purpose methyl methacrylate and unplasticized polystyrene are commented upon. **Properties and machinability of melamine glass cloth laminates** are dealt with by Fuller in "Product Engineering," 1946/**17**/142. Melamine resin has excellent flame resistance and when filled with inflammable materials, such as cotton fabric products of pyrolysis, cause any resultant flame to be self extinguished. New-type GMG laminated insulation has been supplied in the form of sheet, U.S. Navy adopted glass cloth melamine laminates as insulating material for all electrical equipment. Melamine panel board has high tensile and compressive strength and is strongly resistant to bending. It is inimical to fungoid growth and its moisture absorption is low, this last property promoting both dimensional and electrical stability. The author summarizes physical and mechanical properties generally. **Review of developments made in the plastic industry in U.S.A. during the past year** is presented by Rose in "Materials and Methods," 1946/**23**/96. A new cellulose plastic, cellulose Propionate, is announced. It is offered under the trade name of "Forticel," and possesses high impact strength, good dimensional stability and low moisture absorption. It is odourless and is particularly applicable

to kitchen ware. Tests have shown water absorption ranging from 1-1.7 per cent. in an atmosphere of 90 per cent. relative humidity, lineal expansion under these conditions being only 0.4 per cent. Minimum moulding temperature for "Forticel" is given as 465 degrees F., the material beginning to flow at 322 degrees F. Ethyl celluloses have been improved, particularly with regard to impact strength of elevated temperatures. Cellulose ester plastics are still somewhat restricted. Polyethylene is also dealt with by Rose, who notes that it retains its flexibility and toughness over a wide range of temperature. It is the lightest of all commercial plastics. Allyl chloride is a new thermosetting plastic possessing notable high transparency to light.

MISCELLANEOUS

Protective coatings formulated on the basis of liquid plastics are dealt with by Blackmore in "Product Engineering," 1946/**17**/1. Broadly the author examines fields of applicability, present limitations and future possibilities of the system. The close similarity between plastic compositions and paints is commented upon and whilst production methods differ widely in each field, it is pointed out that progress in one sphere invariably lends material aid to the other. The use of alkyd resins, phenolics, ureas, melamines, vinyls, vinylidene chlorides, polystyrenes and silicones in commercial finish formulations is dealt with at some length. **Polysulfide synthetic rubbers** are discussed by Martin in "Product Engineering," 1946/**17**/65. Types A, FA and ST possess the following characteristics: in petrol and petroleum + aromatic fuels, oils and similar solvents, they swell to only a slight extent, they are very stable to oxidation by atmospheric air, have been in the presence of sunlight and ozone. With the exception of type A they have good low-temperature properties whilst their wear resistance and bend strength is adequate. Type A is particularly resistant to deterioration and swell in organic solvents. As compared with natural rubber and other synthetics, however, they possess certain disadvantages, for example, their smell is somewhat unpleasant, they tend to undergo plastic deformation under prolonged pressure and their resistance to low temperature is somewhat mediocre. Type ST, only recently introduced, resembles type FA in its resistance to solvents, but can be vulcanized to give fair resistance to plastic deformation in compression. Applications include paint spray hoses and as coatings and impregnates for felts and fabrics have a wide diversity of uses where resistance to oil, grease and solvents is required. The materials may be used for gaskets and washers. **Redesigned mould for the production of a rubber check valve** is discussed by Wessel in "The Machinist," 1945/**89**/2132. As a result of the change embodied (manufacture could be transformed on a semi-automatic mould press with 50 per cent. saving in rubber) not only was the quality of the work improved, but production costs were reduced.

SOURCES OF REFERENCE.

We wish to remind readers that the sources of reference from which these pages are compiled are not, in general, retained in this office. We cannot, therefore, undertake to supply such originals. Nevertheless, most of the foreign journals referred to are available in the Patent Office Library (Southampton Buildings, Chancery Lane, W.C.2) and in the Science Library (South Kensington). Photo-duplicated copies of articles may be obtained from the Photostat Dept. of the Patent Office.

Wood-flour-filled Phenolic Resins in Tropical Climates

By H. GERLAND*

THE present investigation was undertaken to develop a testing method for the determination of the probable behaviour of a phenolic-plastic in a tropical climate. The greatest demands on plastic components in electrical machines are made by a wet, hot climate with temperatures between 20 degrees and 45 degrees C. and relative moisture contents above 90 per cent. Besides this, desert climates with maximum temperatures of 60 degrees C. are, in particular, dangerous to synthetic resins.

As urea resins do not give satisfactory service in the tropics owing to their tendency to swell and shrink and ultimately crack, emphasis in the tests was laid on phenol-formaldehyde resins, the properties of which, assuming the resin is correctly cured, largely depend on the filler. Now those with wood-flour filler are cheap and easy to mould, but when material of this kind is exposed for some months in the tropical test chamber, the following observations can be made. The mouldings swell, change in dimensions, and the originally smooth and bright surface loses its good appearance; it becomes matt and the structure of the filler used can frequently be recognized. Frequently small blisters and sticky patches are observed; the latter can be caused by the separation of softener, catalyst, or plasticizer, but it may also be due to insufficient curing. Often greyish precipitates become visible, and may be recognized as due to magnesium salts. Mildew formations sometimes occur.

Much more important, however, is the separation of relatively volatile fluids, such as ammonia and acetic acid. These attack moulded-in metallic inserts and may lead to extensive corrosion. Humid atmospheres favour such catastrophes.

Water absorption and correlated swelling of plastics in the tropical test chamber do not provide a complete picture, however. Besides the type of filler and its structure, the resin content and the compression of the material are also influential factors. Thus, fine fibres, well saturated with resin, absorb less water than coarse fibres; 40 per cent. resin mixtures have a greater water absorption than those with 50 per cent., as the filler is, in the latter case, better saturated with resin. Black mixtures absorb more moisture than brown, as, in the latter case, the pigment used is usually of an inorganic nature and not very hygroscopic. For badly cured components, water absorption is invariably unfavourable.

Mildew can form on mouldings with wood flour, textile, or paper fillers; the resin itself does not support it. It has been observed that plastics on the basis of resol resins, in particular with beech-wood-flour fillers, show more pronounced mildew attack than those with novolak resins. The free ammonia always contained in the latter may hinder the formation of such cultures.

Precipitation of magnesium salts on the surface of mouldings may arise partly as a result of magnesia present in the moulding mass, and, again, on account of the free acetic acid. After penetrating as a soluble acetate to the surface, basic salts are finally formed by hydrolysis. The magnesia content usually lies between 0.2 to 2.5 per cent. (The so-called O-masses contain, as a rule, higher magnesia content than the S-masses.)

* "Siemens Zeitschrift," Vol. 23, 1943, pp. 23-27.

The main deterioration to be feared in tropical conditions is corrosion of inserted metal parts caused by ammonia, formic acid, acetic acid and their salts. These can be formed both on the inside and outside of mouldings. The condition for the effective action of these substances on metals is the presence of moisture; heat, simultaneously present in wet-hot climates, merely influences the speed and degree of attack, which is largely dependent on diffusion processes.

In order to find the prime agent of attack, a number of accelerated corrosions tests were carried out on brass, copper, zinc and galvanized iron. Strips of these metals, of approximately equivalent area, were degreased and placed in beakers of about 15 c.c. capacity. At the bottom of each beaker was placed a cotton-wool pad impregnated with 1 c.c. of the medium to be investigated. The metal strip was placed either directly on the pad or suspended in the beaker; in the latter case it came only into contact with the vapours. The vessels were loosely closed and placed in a wet chamber, which, in turn, was located in an oven for 72 hours at a temperature of 40 degrees C. Samples were judged according to their appearance. The following chemicals were examined: Ammonia, acetic acid, formaldehyde, formic acid, phenol, cresol, ammonium-acetate, ammonium-formate, magnesium-acetate, magnesium-formate. The effects of free hexamethylenetetramine of soft beech- and pine-flour, and of damp resin powders were also investigated. Novolak resin with or without " hexa " as accelerator, and resol resin, were also examined.

Results

Ammonia: Acts mainly on copper and brass; the surface becomes darker and, when in actual contact with aqueous solution, basic-salt formation occurs at the surface. Zinc and galvanized iron show, according to the concentration of the ammonia, a more or less pronounced white efflorescence.

Acetic acid: Brass and copper are strongly attacked; formation of basic salts on zinc and galvanized iron and copper alloys.

Neutral ammonium-acetate: Effect weaker than that of acetic acid.

Ammonium-acetate with small NH_3 excess: Effect similar to that of neutral ammonium-acetate.

Ammonium-acetate with excess of acetic acid: Effect on all metals investigated, considerably stronger than with pure acetic acid.

Formic Acid: Effect is considerably weaker than that of acetic acid.

Hexamethylenetetramine:
Ammonium-formate:
Magnesium-acetate:
Magnesium-formate:
} No effect.

Free formaldehyde: Marked white efflorescence on zinc and galvanized iron.

The corrosive media were used in concentrations of 2N, N, $\frac{1}{2}$N, and $\frac{1}{10}$N, and only with concentrations 2N and N were the described effects obtained; with weaker solutions, in general, only colour changes of the metal occurred. Solid substances, such as wood-flour, hexamethylenetetramine, resins, etc., were used in amounts of 1 gm., and no effects were observed.

The results of these rapid tests cannot be correlated, quantitatively, with effects observed under tropical conditions. As, however, standard solutions were used, comparable data were obtained. The most important result was that acetic acid, and, in particular, ammonium-acetate with slight acetic acid excess, showed the strongest effects on metals. This is in conformity with actual observation in the tropics. Phenol-formaldehyde moulding masses containing asbestos, textiles and paper chippings, and ammonia-free accelerators, produce practically no attack on the metals investigated. Wood-flour-containing masses of the same kind give, according to their composition, stronger or weaker effects on metals. O-masses which, due to the presence of wood-flour, always contain free acetic acid, usually attack metals much less readily than S-masses, as they

feature no ammonia-bearing accelerator.

Questions about the origin of the ammonia can readily be answered. It is due to hexamethylenetetramine or materials of similar constitution. In the production of the moulding powder, ammonia is freed from the accelerators by the high temperatures used, whilst more is formed later on during the curing process in the closed mould. Such free ammonia tends to remain in the moulded component, and to evaporate under moist tropical conditions. The simultaneous effect of moisture and heat is, at first, to "loosen up" the moulding, for instance, by swelling, the moulded skin becomes more permeable and allows entrapped gases to dissipate. Moulded parts which had been stored for several weeks in the tropical test chamber show a lower ammonia content than before storage.

Acetic acid is formed from the wood flour by dry distillation, for which suitable conditions exist, on a small scale, even during the mixing of the powder on hot rollers at temperatures up to 130 degrees C. In particular, however, during curing, with temperatures up to about 170 degrees C., such acid formation is hastened.

If the same components be produced from the same powder at the same temperature, but with different curing periods, analysis shows that greater amounts of acetic acid are obtained for longer curing periods. Moulded components with wood-flour fillers, the amounts of free acetic acid in which has been determined before and after storage under tropical conditions, give progressively increasing acid contents. It was observed that pine flour evolved smaller amounts of acetic acid than beech flour.

Moulding powders, types S, S^{x} or O, were next subjected to the action of hexamethylenetetramine, magnesium oxide, magnesium stearate, aluminium oxide, free phenol and free cresol, to determine the part played by them in the splitting off of free acetic acid. "Hexa" and magnesium oxide contained in moulding powder of type S lead to a notable increase in acetic acid formation. "Hexa" is dissociated at curing temperatures into formaldehyde and ammonia, which, in turn, react on the wood flour. The action of magnesium oxide is not so easily explainable, it may, perhaps catalyse the heat dissociation of the wood flour to acetic acid. Free phenols, cresols, and stearic acid show no influence worth mentioning on this process, the last-named, indeed, acts rather as an inhibitor.

Further tests were carried out on fully compounded moulding powders with magnesia contents between 0.5 to 4 per cent. and with "Hexa" contents between 3 and 14 per cent., the resin content being constant in all cases at 45 per cent. Here, again, an increase in the free acetic acid produced was observed. In another series of tests, moulding powders were compounded with varying types and concentrations of resin and with varying amounts and types of filler. In the tropical test chamber powders of higher resin content proved, in general, to react more favourably than those of low resin content, this fact being attributable to the greater degree of saturation of the wood-flour fillers, with, of course, a simultaneous decrease in the amount of wood flour present, and, naturally, a diminution in any possible acetic acid production.

It was by this time assumed that free acetic acid and/or ammonium acetate and ammonia were responsible in the main for corrosion of metallic inserts, and tests were now undertaken therefore to determine a safe limit for these bodies. For determining ammonia or ammonium salts a Schob cup with ribs was produced with moulding temperature 170 degrees C. and curing time of 3 mins. The 3-mm. thick ribs of the cup were broken out and each part again broken into six pieces of about 1 sq. cm. each; the weight of sample was about 20 gm.

The specimen was distilled in a Kjeldahl apparatus with 150 c.c. 15 per cent. sodium hydroxide, rate of distilla-

tion being such that after 30 mins. 100 c.c. of distillate was removed. Ammonia was estimated by back titration with N/10 sulphuric acid. Reproducible results were obtained when conditions of the test were maintained constant. Free acetic acid was estimated by taking a 10-gm. sample in the form of chips passing through a 1-mm. sieve and maintaining as a water suspension for five hours at room temperature in 100 c.c. of water. After the stipulated period of immersion, the suspension was filtered, the precipitate being washed to give a final bulk of 150 c.c. The filtrate was now distilled with 10 c.c. 83 per cent. phosphoric acid at such a rate that in one hour about 600 c.c. would be distilled. The completion of distillation was determined by absence of acidity to litmus paper in the distilled drops. Acetic acid content is estimated by titrating with N/10 sodium hydroxide.

To determine the maximum safe amounts of acetic acid and ammonia, Schob cups as before were made up, using phenolic resin with wood-flour fillers of various concentrations and types. Moulded into the cups were inserts of brass, copper, iron and galvanized iron; the state of the inserts was observed at frequent intervals and any changes in the surface of the plastic were noted during a period of eight weeks' exposure in the tropical test chamber. Somewhat contradictory results were obtained, but it proved possible to show that ammonia up to 0.015 per cent. and acetic acid up to 0.180 per cent. can safely be tolerated. Phenolic resins with wood-flour fillers giving mouldings containing less than 0.015 per cent. ammonia are quite harmless as regards the possibility of corroding metallic inserts. This small amount of free ammonia, incidentally, tends to reduce the quantity of acetic acid present.

Where acetic acid and ammonia contents of mouldings are above these maximum levels, it is not possible to give hard and fast decisions as to their probable behaviour in tropical climates; nevertheless it may be assumed that, with progressively increasing quantities of ammonia and acetic acid, resistance to tropical weathering decreases.

Unfortunately it does not seem possible to establish a commercial standard for wood-flour-filled phenolics for use in the tropics as too many unknowns occur. Moulding temperature and curing time undoubtedly affect the possible contents of free phenol, ammonia, and formaldehyde and exert physical influences, as for example upon density, which naturally affect capacity for water absorption and inter-diffusion in the mass. Wood-flour-filled phenolics for use in tropical climates would, it appears, demand the use of high resin contents, say 50 per cent. or over, with low magnesia contents and, in the case of Novolak resins, no unnecessary excess of hexamethylenetetramine.

So far as the filler is concerned, soft wood is preferable to hard wood. The use of rapid curing resins needing no accelerators presents an opportunity of avoiding the formation of free ammonia. On the finished moulding, acetic-acid values should not be in excess of 0.18 per cent. whilst free ammonia content should not exceed 0.015 per cent.

[It is somewhat regrettable, in view of the importance attached by the author to what might be termed the "chemistry" of the different types of wood flour, that no examination of this was made prior to submitting it to test in conjunction with the plastic materials themselves. If the author's assumption that pyrolysis does occur to some extent during moulding be correct (and there seems no reason to doubt this), there is some reason to suspect that, to a smaller degree, it may also occur during the actual production of the wood flour. This material is an extremely poor conductor of heat, and it is inevitable that fairly high surface temperatures must arise during its manufacture. It is significant that there is a notable difference, under the author's experimental conditions, in the production of acetic acid from a resin-free flour such as beech, and a flour from pine where resin would obviously be produced.]

MOISTURE-PROOF PAPER PACKS

Important Results with New Process

PAPER manufacturers and all concerned with packaging for export will be interested in a new technique for applying polythene coatings to paper and fabrics which produces outstanding moisture resistance.

Attention was first focused on polythene by the wide publicity it received from its use as a dielectric in connection with radar. Films of this thermoplastic have outstanding flexibility and toughness, negligible water absorption, high resistance to the diffusion of water vapour, and are chemically inert. They are not soluble in any of the usual acids or alkalis, and resist chemical attack. This accounts for their use in packing mepacrine tablets, the factory freshness of this sensitive drug being retained under the most exacting conditions.

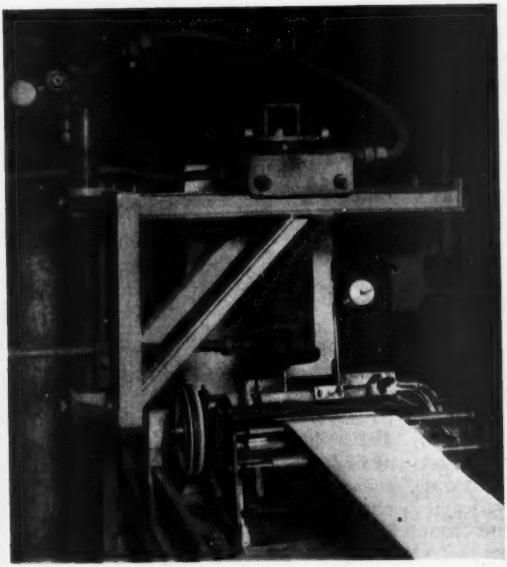
The new process has been developed by Imperial Chemical Industries using grade 200 of "Alkathene," the particular brand of polythene which they manufacture. It is readily adaptable to the needs of the paper trade.

Simplicity of Coating Method

The material is first melted at about 160 degrees C., preferably in an inert atmosphere. After filtering, it is passed into a heated tray, from which it flows on to thoroughly dry paper or fabric. The melt is then spread by means of an adjustable doctor knife, which is heated.

Papers and fabrics thus coated are glossy and attractive, tasteless, odourless and almost water white. They are first-class water vapour barriers under both temperate and tropical conditions. Paper with a coating weight of about 10 lb. double crown has a water vapour permeability of approximately 8 gm./sq. metre/24 hours when tested at 100 degrees F. at 90 per cent. relative humidity, after creasing under a load of 6 lb. per inch of crease. Coated paper can be heat-sealed at 120-150 degrees C. The seal is still extremely strong at a temperature as high as 100 degrees C. Heat-sealed containers will, in fact, hold boiling water. High-frequency heat sealing cannot, of course, be used with this process.

Tests already carried out on a considerable scale indicate that polythene-coated papers and fabrics are likely to find wide industrial applications, including the packaging of many kinds of foodstuffs and chemicals.



Coating machine for moisture-proofing of paper with polythene.

Plastics in Germany

The New Target in Germany is the Science behind the Industries. The following are additional Notes from the Official Reports which can be obtained from H.M. Stationery Office

CIOS XXVI-63.—Rohm and Haas, Darmstadt, Germany. The plant was badly damaged but the unit for making methyl methacrylate monomer is essentially intact. A description is given of the preparation of the monomer for making "Plexiglas" from acetone cyanhydrin (98 per cent pure). The polymerization was carried out by two processes resulting in a "Plexiglas" containing 3 per cent. of dibutylphthalate and pure methyl methacrylate. The process consisted in pouring a 30 per cent. polymer syrup into cells made of thick glass plate. The second or newer process was a mechanical improvement on the first in the preparation of the glass cells. "Plexigum" is methyl methacrylate polymer either in solid (pearl) form, or in organic solvents; either pure methyl methacrylate was used or 7 per cent. of methyl acrylate was added to yield a somewhat softer co-polymer for injection moulding. This was stated to eliminate cracking during moulding. Polymerization was carried out using a dispersing agent, benzoyl peroxide, as catalyst and magnesium carbonate. Rohagite was a co-polymer of methacrylic acid with either methyl methacrylate or methyl acrylamide. This was used as a water-soluble glue for glueing paper. An alkali was added to a water suspension to obtain solution. Acroleinharze is a resin sold as a paste and used in the crease-proofing of textiles.

CIOS XXVII-14.—I.G. Farbenindustrie, Hoechst/Main. Some additional notes contained in this report regarding the subject polyurethane. This product, which is regarded as an improvement on nylon, is looked upon by the I.G. as one of their most important discoveries in recent years. These plastics result from the interaction between di-isocyanates with polyhydroxy compounds. A wide range of physical properties is possible, including some rubber-like substances. They are insoluble in water and other solvents, possess excellent resistance to chemical attack and excellent electrical properties. Vinyl acetate was made at Hoechst by reacting acetylene with ethyl acetate at 400 degrees C., using zinc acetate as the catalyst.

CIOS XVII-68.—Fischer Tropsch Unit at Leipzig Gas Works. One of the many plants in Germany using water gas as a raw material to make fuels, lubricating oils, propane and butane and by-products which were eventually used elsewhere, for the production of chemicals such as long chain acids.

CIOS XXVII-82.—Fischer Tropsch and Allied Processes. This report is the result of a visit to the Kaiser Wilhelm Institute, whose director from 1912 to 1943 was Dr. Franz Fischer. This process, which was carried out in various parts of the country, had one of its largest factories at Sterkrade in the works of Ruhrchemie A.G., which produced some 62,000 tons of hydrocarbon products per year. In addition to these materials, raw chemicals such as ethylene and propylene were converted in their works by the chlorhydrin process or into glycols.

CIOS XXVII-85.—I.G. Farbenindustrie A.G., Ludwigshafen and Oppau. At this factory some 60,000 tons of plastics were made per annum. I.G. did not produce phenol formaldehyde moulding powders. Their phenol formaldehyde resins were made for the manufacture of lacquers and acid-resisting paints. Para tertiary butyl phenol was produced by combining isobutylene with phenol in the presence of a catalyst. The butyl phenol was used

largely for the manufacture of Koresin. Manufactures, including Pollopas, the well-known urea formaldehyde moulding powder, Plastopal, a urea formaldehyde resin converted into lacquers and Melopas, which was made from Melamine. Substitution of Melamine for urea reduces the brittleness of the filler. Kaurit KF and Kauritleim were urea formaldehyde condensations used for textiles and for the glueing of plywood. Igamide A was a condensation product of adipic acid and hexamethylene - diamine. Polythylene (Lupolen) was made at Ludwigshafen in two grades. One—a molecular weight of about 2,000 to 3,000, and the other a molecular weight of about 20,000. Rated production at Ludwigshafen of monomeric styrene in 1943 was 14,000 tons per year. Buna S was manufactured at the rate of 2,000 tons per month. Interesting new vinyl products were vinyl benzoate made from benzoic acid and ethylene and vinyl pyrrolidone which was made from 1.4 butanediol. The vinyl pyrrolidone was polymerized resulting in a water-soluble polymer. This product, known as Kollidon or Periston was used as a substitute for blood plasma.

CIOS XXIX-62.—Investigation of German Plastics Plants.

Part 1 deals with Anorgana G.m.b.H., Gendorf, and with the ethylene and polyethylene made there. The process of manufacture of ethylene by the catalytic hydrogenation of ethylene is given. This method is cheaper than making the gas from potato alcohol. The plant at Gendorf for the manufacture of polyethylene (Lupolen H) was in course of erection, the final product stated to correspond to the I.C.I. material. The general process includes the compression of ethylene to 25,000 lb. per sq. in., the catalyst being oxygen. The plant is designed to produce 5 tons per month. At Gendorf there is also a plant for the production of Luvitherm, an orientated unplasticized polyvinyl chloride film. The polymer is first sieved into a ball mill and then rolled on steel rubber-rollers where the polymer is maintained at 165 degrees for 5-10 minutes at a speed of 11 m. per minute. The material is then cut off the rolls and transferred to a calender for reduction to film. This is a three-bowl vertical machine heated by steam, the top and bottom rolls being adjustable at each end. The thick sheet from the rollers is fed down a chute into the lower nip of the calender, the bowls being maintained at 165-170 degrees. One of the most interesting features in this production is the control of the thickness of the film which is maintained by the use of an electric micrometer. If the film thickness passes outside the tolerance set, coloured lamps on the instrument board warn the operator to hand-set the calender bowls. Another interesting feature is the stretching of the film between two horizontal rollers. The upper roll softens the film by heating it, while the lower one stretches the soft film and then cools it. The plant is designed to make 8-10 tons of film per month. The result of this process is to improve the tensile strength in the direction of stretch to more than double that of the unstretched condition, which is 550 kg./sq. cm. to 2,000 cm. kg./sq. cm. Across the stretch the strengths are diminished.

Part 2 of this investigation includes a description of the works of Dr. Alexander Wacker, Burghausen, where the production of cellulose acetate and polyvinyl chloride was carried out. With regard to the first named, an interesting addition was the production of cellulose acetate wool, the dope solution being fed into gear-spinning pumps and filtered through a candle filter to which spinning jets were attached. The production of vinyl chloride monomer is normal, that is from acetylene and hydrochloric acid, an interesting point being the use of dry hydrogen chloride made by thermal cracking of tetrachloroethane. The production of the polymer at this plant is by the granular polymerization batch process. The charge for an autoclave being 600 lb. of monomer, 13,200 lb. water, 8.8 lb. of benzoyl peroxide as a 30 per cent. water solution; the emulsifier used is an 85 per cent. hydrolized polyvinyl acetate. This is interesting since normally

sulphonic salts are used elsewhere in Germany. The polymerization temperature is 37-40 degrees C., which is maintained for 50 hours. The product is not a true emulsion but a suspension of polymer in water. The charge is then fed into a continuous centrifuge and then to a continuous dryer. The dried P.V.C. is then ground in a mill to size.

Vinyl acetate.—This plant has a capacity of 250 tons per month. The raw materials, acetylene gas and 99.8 per cent. acetic acid, are purified especially with regard to moisture. Both are brought together in an evaporator, the gases thence passing through two heat exchangers, the temperature rising to 160-190 degrees C., then passing through the converter over the catalyst which is activated carbon impregnated with zinc chloride. The crude monomer condensate collected therefrom contains approximately 40 per cent. vinyl acetate. This passes into a fractioning column in which is added hydroquinone as stabilizer. The final product is 99.5 per cent. vinyl acetate. The polymerization plant is carried out in four ways, namely, solvent, emulsion, suspension, or block.

Polyvinyl alcohol—30 tons per month, polyvinyl acetal 5 tons per month, polyvinyl butyral and polyvinyl chloride 10 tons per month, were also manufactured here. The last named was sold for lacquers, adhesives, and artificial shoe soles. Dr. Wacker was probably best known originally for his artificial shellac resin; this was made from acetaldehyde by heating with caustic soda under reflux. Some interesting uses of polyvinyl chloride and polyvinyl alcohol are also given in this section, among them being the production of bicycle tyres, shoe soles, raincoats, driving belts, laces and cords, hammer heads, gloves, petroleum hoses, glider tow ropes, etc.

Part 3 deals with the Munich area targets, the greater number of which, including Knoll A.G., Lignin G.K., Jos. Ernst, Rudorf Hacklechner, Edmund Janich, Franz Unterluganer and Otto Perutz were badly damaged and technical information could not be obtained. At the works of Dr. Alexander Wacker, in Munich, vinyl acetate was made for polymerization, using zinc chloride, although it was also stated that zinc acetate is the better catalyst. An interesting statement obtained here was the fact that copolymers of vinyl chloride and vinyl acetate did not give high molecular weight polymers. A mixed polymer with vinyl chloride always reduces the thermal resistance. Furthermore, the molecular weight of P.V.C. is related to the insulation properties, resistance rising with the molecular weight. P.V.C. was largely used as a leather substitute, the plasticizer (tricresylphosphate) for shoe soles was 50/50 by weight. With regard to polyvinyl acetate for adhesive purposes, a low molecular weight polymer (5,000-10,000) was best. As the molecular weight increases, the adhesive power decreases.

Part 4 deals mainly with an interview with Dr. Otto Jordan, who is a member of the I.G.; he gave information on the following points. The various grades of polystyrene are as follow: Grade 2 has a melting point below 65 degrees, and was plasticized with dibutyl phthalate. It was developed by one firm for coating ammunition and grenades, and was also used as a vehicle for luminous paints inside tanks because of its waterproof qualities. Grade 3, with a melting point of 65-70 degrees, was produced at the rate of 350 tons per month for injection moulding. Grade 4, with a melting point of 70-75 degrees, is more heat-resistant than Grade 3. Grade EN, with a melting point of 80-85 degrees, is a copolymer of 70 per cent. styrene and 30 per cent. acrylonitrile; the melting point can be raised to 100 degrees C. by the addition of 0.1 per cent. divinylbenzene. The use of this special grade was for the production of type for printing, as the shrinkage was very low. Grade B, produced at the rate of 1 ton per month, is a copolymer of styrene with 30 per cent. butyl acrylate. It gave a film more flexible than any of the others. Although I.G. did not produce thin sheets from polystyrene, the Norddeutsche Seekabel developed

machines and a product called Styroflex, which was a straight polystyrene made into foils and stretched to get improved qualities. Another interesting development was the grinding of leather scrap with Acronal or polyvinyl acetate emulsions. Acid or alum was added to the beater precipitating the emulsion in the fibres. The latter was then made into a cardboard-like structure, which was used for the inner soles of shoes.

Part 5 deals with Rohm and Haas, of Darmstadt, who were the sole producers of methyl methacrylate in Germany. They had two plants, one at Darmstadt producing 18,000 square metres of Plexiglas per month, and the other at Mittenwalde, producing 35,000 square metres per month; the thicknesses varied between 0.5-50 mms. In addition, 12-15 tons per month of moulding powder were produced during 1943, and dental powder was produced at the rate of 15 tons per month. The monomer was produced by the standard acetone cyanhydrin method. Butyl methacrylate was also made by a similar method, the ester containing tannic acid as an inhibitor. Methyl methacrylate polymer in granular form was manufactured by this company for dental purposes, and for injection moulding for the production of electrical parts, cover lights, compasses and so on.

Rohagit is an alkali-soluble copolymer made with 65 per cent. methacrylic acid and 35 per cent. methyl methacrylate. Its main use appears to be as a thickening agent for emulsions for stiffening fabrics, and as an emulsifying agent.

Part 6 deals with Wacker and Doerr, compression moulders, of Niederramstadt. Employs 500 and presses with 200 tons highest capacity.

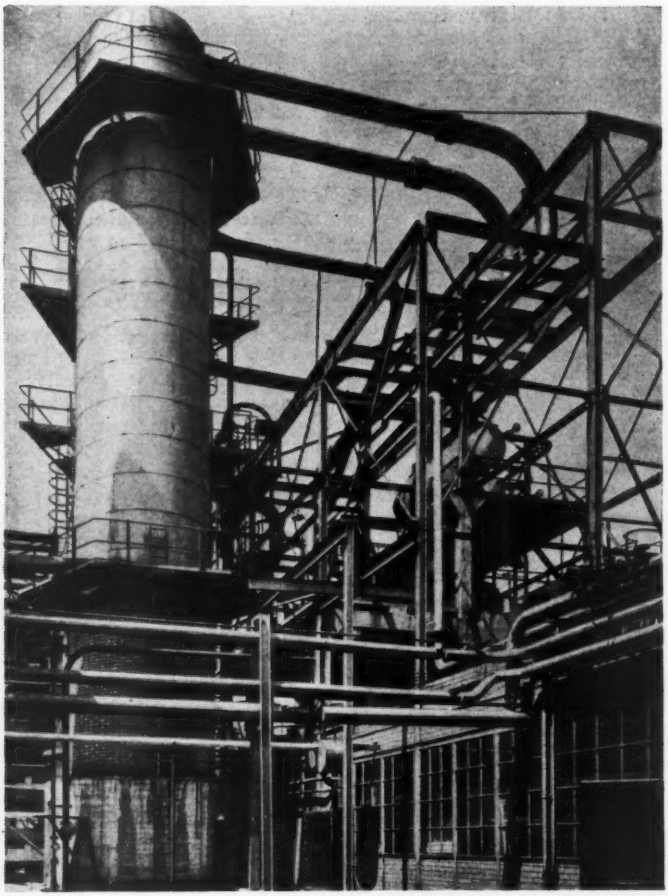
Part 7 deals with the I.G. Farbenindustrie of Ludwigshafen. Much of the information enclosed therein has been already given, but the following applications are worth detailing. The method of applying P.V.C. as a lining to vats is as follows:—The metal surfaces are cleaned free from rust and then degreased and painted with adhesive. This adhesive is made by dissolving Igelit PC (chlorinated P.V.C.) and methylene chloride. The solvent is evaporated by heating and the final sheet pressed into place, while the adhesive surface is hot and tacky. Joints are made by blowing hot air on to the two agents to be joined and using a metal rod or wire to push the two surfaces together. Bristles were made from P.V.C. in a screw extruder, but the bristles were not stretched. Only 1-2 per cent. of plasticizer is added to Igelit PCU; the lubricant was octadecyl alcohol.

Part 8.—Dr. K. Raschig's work on the phenolic resins is well known to all scientists and the description of his works at Ludwigshafen is, therefore, most interesting. The firm distils coal tar, the main products therefrom being cast phenolics in block, rod, and sheet form, lacquer resins and moulding powders. The output of cast phenolics is (Dekorit) 40-50 tons per month. Heat-hardening resins, sold in aqueous or alcoholic solutions, were produced at the rate of 200 tons per month (based on solid content), while the Novolak type was produced at the rate of 150-200 tons per month. These were used as heat-hardening lacquers and as glue for plywood or in paper making.

Moulding materials using wood-flour, slate powder and china clay as fillers were produced at the rate of 400 tons per month. A 100 per cent. moulding resin, Vigopas, was also originally made but has been discontinued. Moulding powders were made by a continuous process; the resin is ground (with hexamethylenetetramine when this is used) and is then mixed with the fillers and other ingredients in a large blender. The mixture is then transferred to mixing rolls, the feed here being of the screw type, and to a vibrating shute which delivers the material to the centre of a pair of rotating rolls. The sheet forms on both sides of the front roll of which about 7 ins. from the end two grooves are cut and two wheel-type cutting knives are located. When the moulding sheet reaches the wheels it is stripped off. Final grinding is done in a hammer drill. Different grades of material are controlled by variations in the feel of material to the roll.

Plastics *from* Petroleum

PETROLEUM always has had a very definite news value, but at the present time in this immediate post-war period it fills the minds of technicians and laymen alike more than ever. The adroit manœuvrings of politicians and delegates at conferences appear to be



By
H. RONALD FLECK,
M.Sc., F.R.I.C.

The two photographs shown, illustrate the distillation plant and (right) the Edeleanu (sulphur dioxide treatment) plant of the Manchester Oil Refinery. While production here does not embrace many of the chemicals described by the author, it is hoped that British refining will eventually do so.

directed at control of petroleum deposits and pipe-lines to refineries. Roughly speaking, the larger oil deposits come within the orbits of three of the main Powers; the U.S.A. controlling her home and Continental resources; the U.S.S.R. controlling her home resources and at the moment some of the Rumanian oil-fields; and the British Empire controlling Arabian and East Indian deposits within the sterling bloc. We have, therefore, a dollar area of oil deposits, a sterling area of oil deposits, and a closed system operating within the U.S.S.R. The finances of the world are in a chaotic state due to the unprecedented expenditures incurred during the war, and, in particular, the finances of this country are at a very low ebb. In order to purchase petroleum and its products we must buy either in the dollar area or the sterling area. To buy petroleum in the dollar area will necessarily involve this country in a vast borrowing campaign, carrying with it the acceptance of the Bretton Woods proposals for an international monetary fund, the setting up of gold once more as a fiduciary standard, and a limitation of the preference granted to members of the sterling area. Withdrawal from the dollar area and exclusive buying of petroleum within the sterling area is not practicable because of foodstuff requirements from the U.S.A., and we see that an apparent impasse has been created, retreat from which will require most delicate handling and a very rapid stocktaking on logistic principles.

Deposits of crude oil occur within our own shores, but at the moment the extent of these deposits is not known with any great degree of accuracy. During the war years these deposits have been worked systematically for the first time, with the result that an annual crude oil production of some 100,000 tons has been achieved. But this amount represents only about 1 per cent. of our annual requirements of crude oil, and is equivalent to about 10 tankers from the U.S.A. Various wild assumptions are sometimes made as to the deposits in this country, but at the moment no accurate figures are available, although a detailed survey is being made under the auspices of the appropriate Ministry. Indigenous oil,

then, is a proven fact, but it remains to be seen whether the amount available will ever be sufficient to make us independent of outside sources, and also whether the quality of the oil will lend itself satisfactorily to treatment in the refinery.

We must remember that although the world output of crude oil has risen from about 20,000,000 tons in 1900 to 270,000,000 tons in 1938, the mechanization of the world is steadily increasing and the call for more oil becomes insistent and urgent. High-volatility spirit, petrol or gasoline, is the greatest necessity in this era of internal-combustion engines, yet less than 25 per cent. of the crude oil is immediately available as motor spirit, so that increasing production of petrol led, in the past, to increasing production of relatively unwanted heavy oils of the kerosene type. These oils had to be sold in competition with coal as fuels on the basis of a declared calorific value and as such represented a heavy expense to the oil companies. It is as well to digress here for a moment to examine the technical basis of the oil companies. It was realized at a very early stage in the development of the industry that unless adequate research work was undertaken, the industry would be unable to run on economic lines. The oil industry lives by the research work carried out by its technicians and they serve their industry well. The quality of the research work carried out under the ægis of the oil companies is amazingly high and represents one of the greatest modern contributions to the science of organic chemistry. The research work falls naturally into two main divisions, fundamental or basic reaction principles and utilization. This combination of conceptions has enabled the companies to understand the molecular construction of crude oil and to re-arrange the molecules to their best advantage.

As obtained from the wells, crude oil is a complex mixture of hydrocarbons, both gaseous and liquid, containing combined sulphur. The gaseous portion of this mixture consists of the lower saturated hydrocarbons such as pentane, hexane, heptane, etc, and the higher boiling fractions are complicated mixtures of saturated and unsaturated hydrocarbons. This heterogeneous mixture of organic liquids is to some extent separated into fractions by the process known as refining. Normally, refining is carried out in the country of origin of the oil, either at the well head or at the end of a pipeline to the nearest port or sea coast town. The refined products are then shipped to the ports of overseas customers or delivered by tank wagons for internal usage in the country of origin. In this country a courageous attempt to carry out refining of oil has been made, with considerable success, by the Manchester Oil Refinery, an independent organization outside the ring of oil companies.

The author has recently had an opportunity of visiting the works operated by this concern, and a detailed description of the methods adopted will be of value in the development of the main theme of this article.

Refining at Manchester Oil Refinery

The crude oil is known as "topped" oil; it has been freed of the dissolved gases and most of the volatile gasoline and kerosene fraction by a straight atmospheric distillation. The resulting topped crude oil is shipped in tankers straight up the Manchester Ship Canal and is pumped directly from the ship into storage tanks ashore. From these tanks the oil is pumped into the atmospheric distillation chamber, where any residual gasoline and kerosene is vaporized by heating, the vapours being condensed and run off into storage. The crude oil is now distilled in a partial vacuum, the vapours being condensed in a fractionating tower. The heavier molecules of higher viscosity oil condense low down in the column and flow from side pipes into receivers, lighter molecules condense at a higher level, and a third fraction condenses near the top of the column. Heat exchangers are used in this distillation, the incoming crude oil being led in counter current pipes through the

hot distillate pipes. The cold crude oil is thus preheated by the distillate, which is in turn cooled, the heat used in the process being thus conserved and running costs of the plant being reduced. The residue in the still is blown with steam to remove all volatile matter and then pumped out as fuel oil. The three fractions from the fractionating column form the basis of lubricating oil, but first the unsaturated hydrocarbons must be removed to avoid undue gumming during engine use. Advantage is taken at this stage of the reaction between unsaturated hydrocarbons and liquid sulphur dioxide, and the fact that the sulphonated bodies thus formed are soluble in the liquid sulphur dioxide. This process is known as the Edeleanu process, and is operated on a counter-current system. The particular fraction under treatment is pumped into a reaction chamber and the solvent pumped in in such a way that a very intimate mixture is achieved. After settling and separation into two layers, the solvent is pumped off to react with more crude oil distillate, the first treated oil fraction being again mixed with fresh liquid sulphur dioxide; the general direction of the oil is downwards and of the solvent upwards. The "raffinate," or extracted oil, passes on to the dewaxing plant, where a small quantity of amorphous wax is removed by adding benzole and a crystalline wax, freezing the mixture and filtering off the benzole-crystalline wax-amorphous wax solid system under suction. Residual benzole and sulphur dioxide are removed from the dewaxed oil by evaporation, and the resulting lubricating oil pumped forward to storage or to further chemical refining. The sulphur dioxide extract is evaporated to recover the solvent and the complex residue of sulphonated hydrocarbons reserved for subsequent refining.

In the manufacture of transformer oils, white oils and liquid paraffin for medicinal purposes, the raffinate is further treated with oleum, concentrated sulphuric acid containing 20 per cent. of sulphur tri-oxide—which converts portions of the oil into petroleum sulphonates. These sulphonates are extracted with alcoholic caustic soda, and the resulting products have very great value as emulsifiers. The oil is finally treated hot with clay and filtered in filter presses.

Formation of Gaseous Products

As we shall see later in this article, the gaseous products of the oil wells are of paramount importance to the plastics industry, and these gaseous products are missing from the crude oil delivered to this Manchester factory. The research department have evolved a process depending on the controlled heating of oil in the presence of a catalyst, which enables the larger oil molecules to be broken down or "cracked" into smaller molecules of gaseous type having an unsaturated structure. By this process the oil is broken down into a 50/50 mixture of gaseous and liquid hydrocarbons, the gases being largely methane, ethylene and propylene, and the liquid consisting largely of aromatic hydrocarbons having a cyclic structure, such as benzene, toluene and cyclopentane. These aromatics are in a high state of purity and will eventually form the basic raw materials for plastics manufacture. This pioneer work is of immense interest to the home plastics industry, and the author is indebted to the Manchester Oil Refinery for permission to publish this short account of their endeavours in this field of modern alchemy.

The fact that crude oil contains only about 25 per cent. of highly volatile hydrocarbons suitable for use as fuel in internal-combustion engines has led to the widespread introduction of "cracking" processes in which the higher hydrocarbons are broken down into smaller-sized molecules having greater volatility. The cracking process is chemical in nature, being the application of temperature and pressure under rigidly controlled conditions. The cracked petroleum can be re-formed into saturated hydrocarbons by suitable adjustment of the conditions, the ratio of olefines (unsaturated hydrocarbons) to paraffins (saturated hydro-

carbons) being roughly one-third olefines to two-thirds paraffins. Hydrogen is also set free in this cracking process, and the general type of reaction is exemplified by the following equations showing the production of (a) ethylene from ethane, (b) ethylene or propylene from propane, and (c) ethylene, propylene or butylene from butane.

(a) $CH_3CH_3 \longrightarrow CH_2 = CH_2 + H_2$

(b) $CH_3.CH_2.CH_3 \longrightarrow CH_2 = CH_2 + CH_4$
or $CH_3.CH = CH_2 + H_2$

(c) $CH_3.CH_2.CH_2.CH_3 \longrightarrow$
$\longrightarrow CH_2 = CH_2 + CH_3.CH_3$
or $CH_3.CH = CH_2 + CH_4$
or $CH_3.CH_2.CH = CH_2 + H_2$

Secondary reactions can also be brought about if the conditions chosen are fairly mild, as, for example, the production of butadiene, propylene methane and hydrogen from butylene (in turn produced from butane)

$2CH_3.CH_2.CH = CH_2 \longrightarrow CH_2 = CH.CH =$
$= CH_2 + CH_3.CH = CH_2 + CH_4 + H_2.$

The unsaturated gaseous hydrocarbons produced by the controlled cracking of petroleum are exceedingly reactive in the chemical sense and can form the basis of many chemical syntheses, leading up to the formation of plastic materials. It will be sufficient for the purposes of this article if we consider four of these gases, namely, ethylene, propylene, butylene and butadiene.

Ethylene.—$CH_2 = CH_2$. Colourless gas, having a faint sweetish odour. It will unite directly with chlorine and bromine to form ethylene dichloride and ethylene dibromide, respectively.

Ethylene dichloride may be chlorinated directly, in the presence of a metallic catalyst to give 1.1.2-trichlorethane $CH_2Cl.CHCl_2$ from which vinylidene chloride (1 : 1-dichlorethylene) may be prepared by the action of an aqueous suspension of calcium hydroxide:—

$2CH_2Cl.CHCl_2 + Ca(OH)_2 \longrightarrow 2\ CH_2 =$
$= CH.Cl_2 + CaCl_2 + 2H_2O$

Vinylidene chloride is a clear, colourless liquid boiling at 31.7 degrees C., which is capable of chain polymerization to form a thermo-plastic polymer.

Vinyl chloride may be obtained by the action of alcoholic potash on ethylene dichloride $CH_2Cl.CH_2Cl + KOH \longrightarrow$
$\longrightarrow CH_2 = CH.Cl + KCl + H_2O.$
vinyl chloride thus produced is the raw material for the preparation of polyvinyl chloride.

Ethylene glycol—a dihydric alcohol sometimes used in the preparation of flexible alkyd resins—is obtained by the controlled oxidation of ethylene by aqueous permanganate solutions.

$CH_2 = CH_2 + O + H_2O \longrightarrow$
$\longrightarrow CH_2(OH).CH_2(OH).$

Hypochlorous acid in aqueous solution converts ethylene into the corresponding chlorhydrin $CH_2 = CH_2 + HOCl \longrightarrow$
$\longrightarrow CH_2Cl.CH_2(OH).$

Ethylene oxide $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > O$ is formed by the action of potassium hydroxide on ethylene chlorhydrin by elimination of the elements of hydrogen chloride.

The gaseous ethylene can be polymerized at about 500 degrees C. and 15 atmospheres pressure to give good yields of butene $CH_3.CH_2.CH = CH_2$ and under controlled conditions cyclization and polymerization of ethylene to benzene has been shown to be quite practicable. Chain polymers of ethylene are widely prepared in this country by subjecting gaseous ethylene to very high pressures (about 1,200 atmospheres) at temperatures varying from 100 degrees to 200 degrees C. The polymers obtained in this process are thermoplastic and have excellent electrical characteristics; they can be injection moulded and have the advantage that low injection pressures only are necessary during the moulding cycle.

Probably one of the most interesting uses for ethylene will be in the preparation of styrene. Ethylene can be readily converted into ethane by reduction, and into ethyl chloride by chlorination of the ethane. The next step in the synthesis is the application of the Friedel-Crafts reaction, ethyl chloride being passed into

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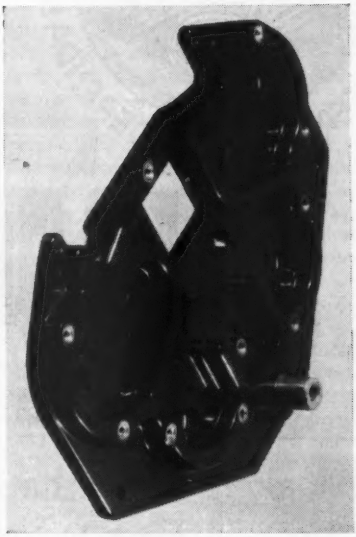

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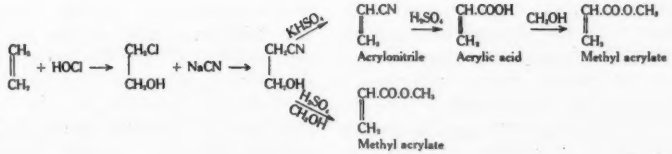
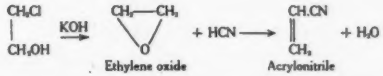


benzene in the presence of anhydrous aluminium chloride. Ethyl benzene is produced in this manner, and is then subjected to a cracking process to eliminate hydrogen from the side chain, the product being phenyl ethylene or styrene as it is more usually termed. The cracking process is carried out continuously, ethyl benzene being passed through iron tubes heated at 650 degrees C., the issuing vapours are chilled to crystallize the styrene which is then filtered from unchanged ethyl benzene. The ethyl benzene is returned to the cracking tubes and the cycle repeated.

Considerable research work has been carried out on this process and a new method has been developed for the direct union of ethylene and benzene working at small positive pressures and temperatures in the neighbourhood of 90 degrees C. Anhydrous aluminium chloride is used as catalyst and the ethyl benzene produced is extremely pure. Since both ethylene and benzene can be produced from petroleum by cracking, styrene production can now be independent of coal production. Polystyrene is a very important thermoplastic material and its production from petroleum should make it very much more freely available than has been the case.

Another important reaction of ethylene leads to the formation of one member of the acrylate series of thermoplastic materials. Ethylene chlorhydrin, formed either by the direct union of gaseous ethylene and hypochlorous acid, or by passing hydrogen chloride into ethylene glycol at 100 degrees C., will react with sodium cyanide to form the corresponding hydroxycyanide or cyanohydrin. Dehydration of the cyanohydrin leads to the formation of acrylonitrile, a most important intermediate in the production of synthetic elastomers of the Perbunan type. Nitriles can be hydrolized by means of concentrated sulphuric acid to carboxylic acids, acrylonitrile yielding acrylic acid under these conditions. On esterification with methyl alcohol methyl acrylate is formed. Methyl acrylate is usually produced from ethylene cyanohydrin by simultaneous dehydration, hydrolysis, and esterification with concentrated sulphuric acid and methyl alcohol. The equation for these reactions is shown above.

Acrylonitrile can also be produced by the direct union of ethylene oxide (prepared by the action of caustic potash on ethylene chlorhydrin) and hydrocyanic acid.



Propylene.—$CH_3.CH=CH_2$. A colourless gas having similar properties to ethylene. It undergoes most of the reactions detailed above for ethylene forming propylene oxide, propylene glycol, propylene chlorhydrin, etc.

Of interest from the plastic point of view is the preparation of glycerol—used in the manufacture of alkyd resins—from propylene. Propylene unites directly with bromine to form propylene dibromide, and this, in turn, is brominated in the presence of iron to the corresponding propylene tribromide. The bromine atoms are displaced by acetyl groups with the aid of silver acetate, yielding propenyl or glyceryl triacetate. This substance is then hydrolized to glycerol by means of aqueous alkali. Although this synthesis is practicable and has been used for preparing glycerol during war-time, it is

doubtful whether it can compete on a cost basis with the glycerol obtained as a by-product of soap manufacture.

When propylene reacts with hypochlorous acid the chlorhydrin is formed. The removal of the elements of hydrogen chloride from propylene chlorohydrin gives rise to an unsaturated alcohol—allyl alcohol $CH_2 = CH.CH_2(OH)$—the esters of which show great promise in the plastics field. These esters are capable of polymerization, using benzoyl peroxide as catalyst, to form long chain polymers having thermoplastic properties and good electrical characteristics.

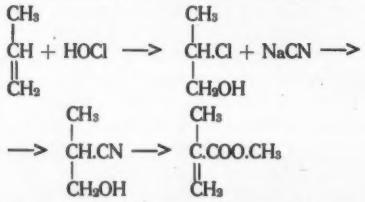
Propylene is convertible into iso-propyl alcohol by union with hydrobromic acid, and subsequent removal of the bromine atom with moist silver oxide. It is probable that industrial manufacture of this alcohol will eventually be adopted, owing to its importance as a solvent.

An interesting extension of organic syntheses from propylene permits of the preparation of methyl methacrylate by the following route:—

Propylene—>propylene chlorhydrin—> iso-propyl alcohol—>acetone—>acetone cyanohydrin—>methyl methacrylate.

This route depends on the oxidation of iso-propyl alcohol to acetone by means of chromic acid, treatment of the acetone with hydrogen cyanide to form the cyanohydrin and the subsequent simultaneous hydrolysis and esterification of the cyanohydrin to the methyl methacrylate.

Similarly, methyl methacrylate can be prepared directly from propylene chlorhydrin via the cyanohydrin, which is simultaneously dehydrated and esterified.



In view of the great reactivity of propylene, it is probable that many more developments will quickly follow the industrial preparation of the gas in considerable quantities. Chain polymers of the type of polythene from ethylene are theoretically possible in the case of propylene, and indeed from all of the gaseous members of this homologous series.

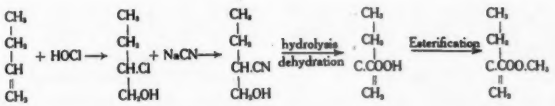
Butylene.—C_4H_8. There are three possible isomeric butylenes—normal butylene $CH_3.CH_2.CH=CH_2$, β-butylene $CH_3.CH=CH.CH_3$, and iso-butylene $\begin{matrix}CH_3\\CH_3\end{matrix}>C=CH_2$. All three are colourless gases, the first two being derived from normal butane, and the third from iso-butane. They exhibit the normal reactions of olefines, combining with chlorine, hypochlorous acid, hydrobromic acid, and forming oxides and glycols.

Iso-butylene has found industrial application through its co-polymer with butadiene, giving rise to the well-known synthetic elastomer Butyl rubber.

As in the cases of ethylene and propylene, the butylenes are very reactive and will undoubtedly form the basic raw materials for many new syntheses of industrial significance.

Iso-butylene will unite directly with hydrogen chloride to form the tertiary butyl chloride $(CH_3)_2CH.CH_2Cl$. By making use of the Friedel-Crafts reaction between tertiary butyl chloride and phenol, the very valuable subsfituted phenol, para-tertiary butyl phenol, is produced from phenol and iso-butylene in the presence of anhydrous aluminium chloride as a catalyst. By a similar process to that used in the case of propylene iso-butyl alcohol, or iso-butanol can be prepared from iso-butylene. Iso-butanol has valuable solvent properties, and such esters as the acetate and propionate have found favour in the lacquer industry.

Normal butylene will unite directly with hypochlorous acid to form the corresponding chlorhydrin, which is converted into the cyanohydrin by treatment with sodium cyanide. Simultaneous



dehydration, hydrolysis and esterification of the cyanohydrin with concentrated sulphuric acid and methyl alcohol gives rise to methyl ethacrylate, as shown in the equation above.

Butadiene.—$CH_2 = CH.CH. = CH_2$. Butadiene is a gas at ordinary temperatures and pressures, but forms a colourless liquid boiling at −4.5 degrees C. when cooled. It is exceedingly reactive, as might be expected from a substance containing a conjugated double bond, and its main industrial significance lies in its polymers and co-polymers, which are the basis of the synthetic elastomers (or rubber-like substances) of the Buna and Perbunan types. There are several methods of preparing butadiene, but the main industrial method, particularly from the point of view of this article, is from butane derived from petroleum, via butylene.

Butane can be dehydrogenated at atmospheric pressure by passing it over an activated catalyst of chromic oxide on alumina, the catalyst being maintained at a temperature of 590-600 degrees C. The resulting product, butylene, is obtained in a yield of 40 per cent. per passage over the catalyst. Butylene has only one double bond and must be further dehydrogenated to obtain the conjugated structure of butadiene. This is accomplished by passing the butylene gas over a metallic oxide catalyst supported on alumina, at reduced pressure and a temperature of 500-700 degrees C., depending on the type of catalyst employed.

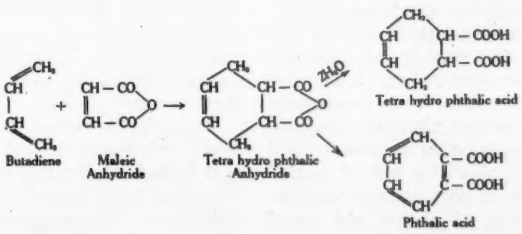
The reactions leading to this formation are shown in the equation—

$$CH_3.CH_2.CH_2.CH_3 \longrightarrow$$
Butane
$$\longrightarrow CH_3.CH_2.CH = CH_2 + H_2 \longrightarrow$$
normal-Butylene
$$\longrightarrow CH_2 = CH - CH = CH_2 + H_2$$
Butadiene.

In view of the reactivity conferred on butadiene by the conjugated system, it is probable that many more uses will be found for it in organic syntheses and in the plastics industry. As an example of this reactivity, butadiene will undergo the Diels-Alder diene reaction, forming an additive compound, tetrahydrophthalic anhydride, with maleic anhydride. The possible substitution of this material, for, or dehydrogenation to, phthalic anhydride for use in the preparation of alkyd resins or plasticizers for thermoplastic materials is obvious. The reactions leading to this formation are shown in the formula below.

Before leaving the subject of these reactive petroleum gases, we must briefly deal with certain reactions which may have far-reaching importance in the future.

Propylene will give rise to acetone via iso-propyl alcohol, and this material is of considerable importance to the plastics industry apart from its value as a solvent. Acetone will condense with many



aldehydes in the presence of milk alkaline catalysts to give resins which are insoluble in organic solvents. These resins have been suggested as alternatives to the methacrylate series, since they can be produced more cheaply. Another interesting possibility of utilizing acetone is based upon the formation of ketene from acetone by passing the vapour through a tube partially filled with earthenware at a dull red heat.

$$\underset{\text{Acetone}}{CH_3.CO.CH_3} \longrightarrow \underset{\text{Ketene}}{CH_2 = C = O} + \underset{\text{Methane.}}{CH_4}$$

Ketene will react with water to form acetic acid and acetic anhydride, both of which are used to a large extent in the cellulose plastic industry. Ketene will also polymerize spontaneously into an oily polymeride and will undergo many reactions of interest to the chemist.

Just prior to the war, announcements were made in American technical journals concerning a new series of industrial chemicals—the nitro-paraffins. These nitro-paraffins are prepared from the paraffinic hydrocarbons derived from petroleum—methane, ethane, propane, butane, etc., and claims were made for the nitro-derivatives as solvents, and intermediate products in chemical syntheses. Not more than research quantities became available in this country at the time of the anouncement, but it is quite possible that the reactivity of these nitro-paraffins may be utilized to good purpose by plastics chemists. The nitro group is readily reduced to the amino group, and conjectural examples such as the reduction of a dinitro-hexane to hexamethylene diamine—an intermediate in the preparation of nylon—give rise to interesting possibilities.

In dealing with the cracking of petroleum to gas by catalytic means, it was mentioned earlier that 50 per cent. of the cracked material had undergone cyclization to aromatic hydrocarbons such as benzene and toluene. The production of the substances in quantity, and in a high state of purity will, if carried out extensively in this country, supplement the amount of phenol and cresol which is at present obtained almost solely as a by-product of the coal gas industry. Since 10 tons of coal must be burned to produce about 60 lb. of mixed phenol and cresols, any additional amount produced from the aromatization process will be very welcome.

Phenol can be manufactured easily from benzene by two processes—(a) Treatment of benzene with sulphuric acid to give benzene sulphonic acid, the latter being converted into the sodium salt by means of sodium sulphite. The sodium benzene sulphonate is then fused with sodium hydroxide to yield sodium phenate, which on acidification with sulphur dioxide—derived from the sulphite—gives phenol.

$$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$$

$$2C_6H_5SO_3H + Na_2SO_3 \longrightarrow 2C_6H_5SO_3Na + SO_2 + H_2O$$

$$C_6H_5SO_3Na + 2NaOH \longrightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

$$2C_6H_5ONa + SO_2 + H_2O \longrightarrow 2C_6H_5OH + Na_2SO_3$$

(b) Benzene is chlorinated in the presence of iron as a catalyst to give a mixture of mono- and dichlor-benzenes. The monochlor-benzene is obtained by fractionation and hydrolysed by means of sodium carbonate to phenol—

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

$$2C_6H_5Cl + Na_2CO_3 + H_2O \longrightarrow 2C_6H_5OH + 2NaCl + CO_2$$

Cyclo-pentane and cyclo-pentadiene compounds will in all probability also appear in the aromatized liquid portion of the cracked petroleum. These substances can be polymerized.

To complete the survey of the phenolic resin field, formaldehyde can be produced from the methane occurring in cracking gases, via methyl chloride and methyl alcohol. Phenolic resins entirely independent of the coal tar industry are therefore quite feasible.

Probably the largest field at present in which petroleum derivatives find use is that branch of the rubber industry concerned with the manufacture of synthetic elastomers. The scope in this branch is

vast, as can be seen from the following classified list of elastomers.

Group I.—" True " synthetic rubbers or elastoprenes.

A. Simple butadiene polymers.

B. 1. Butadiene – styrene co-polymer. Buna S.
2. Butadiene – acrylonitrile co-polymers. Buna N, Perbunan, Chemigum, Hycar.

C. Substituted butadiene polymers.
1. Polymers of isoprene (methyl-butadiene).
2. Polymers of methyl isoprene.
3. Polymers of chloroprene (Neoprene).

D. Modified butene polymers. Butenes plus small amounts of co-polymerized butadiene or other didefines—Butyl rubber.

Group II.—Synthetic rubber-like saturated elasto-plastics.

A. Polyalkanes.
1. Polybutene – Vistanex.
2. Polyphenylene ethylene – A.X.F.

B. Polyvinyl derivatives.
1. Polyvinyl alcohols – P.V.A. series.
2. Polyvinyl chloride – acetate co-polymers – Vinylites.
3. Polyvinyl chloride – Koroseal B.F., Vinylite Q, Flamenol.
4. Polyvinylidene chloride – Saran.
5. Polyvinyl acetals (a) Polyvinyl alcohol + formaldehyde – Formvar. (b) Polyvinyl alcohol + butyraldehyde – Butvar, Butacite, Vinylite X.

C. Reaction products of aliphatic dihalides and alkali polysulphides.
1. Ethylene dichloride and sodium tetrasulphide – Thiokol A.
2. Dichloro-diethyl ether and sodium tetrasulphide – Thiokol B.

Many of these elastomers have been produced during the war from the gases derived from petroleum cracking, notably Buna S, Buna N, and the Perbunan series, together with quantities of Butyl rubber. These materials were mainly manufactured in the United States of America. Thiokols have been manufactured in this country, as also has polythene from ethylene, although it is probable that the necessary ethylene was derived from sources other than petroleum.

The reactions leading to the formation of Thiokol A are interesting and are sufficiently typical to serve as an example of the general methods adopted in the preparation of synthetic elastomers.

Ethylene dichloride, a liquid boiling at 85 degrees C., is produced by the direct union of ethylene and chlorine. A controlled solution of sodium tetrasulphide (made by dissolving sulphur in sodium sulphide) is poured into a reaction vessel, ethylene dichloride added and the mixture heated with vigorous stirring. The two liquids emulsify and a white latex results in an hour or two. This latex is coagulated by means of acid (a method often adopted with natural rubber latex), the concentration, rate of addition and speed of stirring being carefully regulated in order to obtain a granular product. The granules are washed, filtered and dried.

The future of synthetic elastomers is somewhat problematical since they came into large industrial existence as a matter of military expediency. The necessity to rehabilitate large masses of natives makes it imperative that natural rubber shall again be produced in large quantities. Moreover, the natural product possesses certain advantages over the synthetic substitutes, so that it will regain a position on its own merits. On the other hand, the vast new industry for producing the substitutes cannot be allowed to die out, and it is probable that some equitable distribution between the natural and synthetic materials will be worked out.

The purpose of this article has been to show the possibilities of petroleum in

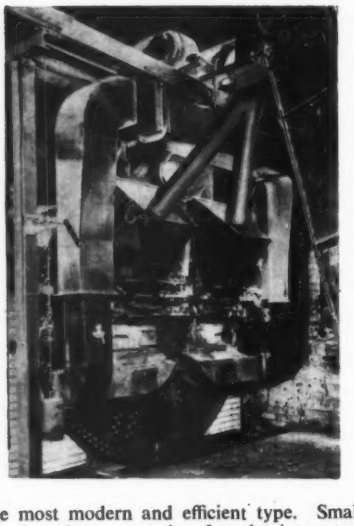
(Continued on page 168.)

PRODUCTION NEWS

Raw Materials, New Plant, Works Organization, Control Apparatus, Research, Personal and Trade Notes

ECONOMICAL STEAM GENERATION.—Three of the chief advantages of mechanical stoking for "Lancashire" and other cylindrical boilers (using coal) are economical steam generation, high rate of evaporation, and elimination of the difficult and laborious operation of hand firing.

What can be accomplished, even by a small installation, is well illustrated by the case of a woollen mill (in England) which has been equipped with a power plant of



the most modern and efficient type. Small plastics plants may therefore be interested. Operation is by a 30-ft. by 9-ft. "Lancashire" boiler working at 240 lb. per sq. in. pressure, and with the steam superheated to 650 degrees F., operating a pass-out steam turbine of 1,125 kw., direct coupled to a turbo-alternator, the mill being driven electrically. Also the boiler is equipped with a large installation of economizers consisting of 160 tubes 11 ft. 6 ins. long, which raise the feed-water from 130 degrees F. leaving the boiler to 300 degrees F. as discharged to the chimney.

This plant runs continuously, day and night, from Monday morning till Saturday midday, being 125 hours of work. The boiler is operated by a "Meldrum" sprinkling-type mechanical stoker with self-cleaning grates and fan forced draught, an electrically driven fan being fixed over the top half of the furnace tubes beneath the grate, combined with a small inclined elevator for the coal.

The performance of the plant is remarkably efficient, and it may be stated that in addition to all the pass-out steam used for heating and process work a certain amount of live steam is taken direct from the boiler for this purpose, since in some cases a relatively high pressure is necessary, whilst the most scientific methods are also employed in connection with the utilization of waste steam and of hot water, especially as regards the condensate. Further, detailed performance records are taken continuously, and, for example, on month to month running the average operation is 7.88 lb. of water evaporated per lb. of coal, which is 74.8 per cent. thermal efficiency, an extremely high figure.

Even more striking is the rate of evaporation of the 30-ft. by 9-ft. boiler, which often averages 12,000 lb. of water per hour per day shift, and in some cases has even reached 14,000 lb., very nearly twice the figure of the average "Lancashire" boiler plant.

Messrs. Meldrums, Ltd., Timperley, near Manchester, make a wide range of equipment for the operation of cylindrical and other boilers, and were pioneers in the use of steam jets for forced draught. Their equipment includes hand-fired forced-draught furnaces with either steam or jet or fan draught, sprinkler stokers, etc.

I.C.I. DEVELOP NEW RESIN.—The development of a new type of synthetic resin is just announced by the Plastics Division of Imperial Chemical Industries. This resin has been designed for use as a contact or low-pressure laminating resin and, in addition, has possibilities for general-purpose impregnating and casting.

British manufacturers have long felt the need for home-produced "contact pressure" resins of this kind. Their value for special applications was early recognized, and in America they have been widely used, especially by the aircraft industry. Up till now work on them has largely been kept secret.

The new resin makes possible the production of large tough laminates of complicated design with simple equipment and at economic cost. For that reason, a wide range of applications is forecast for it.

Contact pressure resins are specially suitable for the construction of shaped laminated articles, making use of fabric or paper. Where great strength is required, glass fabric has been found to give good results. A mould or former is required, on which the shaped article is built up, and the very light pressure needed can easily be applied by the rubber-bag technique. With shaped articles, the fabric is cut into tailored pieces, so that it fits closely to the "former" without creases. The resin, which is a brown, viscous liquid, has a small quantity of catalyst added to it before use, and is then applied to the fabric by brushing or impregnating in a bath. A resin content of from 40-50 per cent., depending on the fabric, is usually employed. Curing takes up to half an hour at a temperature of about 100 degrees C.

BRITISH PLASTICS FEDERATION announce that a number of C.I.O.S. and B.I.O.S. reports of teams on German factories manufacturing plastic materials have been placed in the Library of the British Plastics Federation, and are available for consultation by both members and non-members of the Federation.

BRITISH GEON LTD.—With the view to extending their plastics manufacture The Distillers Company Limited, in conjunction with B. F. Goodrich Chemical Company of Cleveland, Ohio, has promoted a Private Company which has been incorporated in England under the title of British Geon Limited with a capital of £500,000 consisting of 225,000 5 per cent. Preference Shares and 275,000 Ordinary Shares, all of £1 each.

The primary object of the new Company is the manufacture in the United Kingdom of polyvinyl chloride and co-polymers.

The first Directors are:—Sir Walrond Sinclair (Chairman), Mr. John L. Collyer, President of the B. F. Goodrich Company, Mr. William S. Richardson, President of the B. F. Goodrich Chemical Company, Mr. C. G. Hayman, Mr. L. A. Elgood, Major C. J. P. Ball and Mr. H. H. Woolveridge (The Distillers Company Limited).

BRITISH STANDARD SPECIFICATION for Definition of Technical Mouldings (Plastics) (B.S. No. 1253 : 1945).—The Mark Committee of the British Standards Institution has drawn up in collaboration with the British Plastics Federation a certification scheme applicable to plastic materials and to products made of plastics. This mark may be used under licence from the B.S.I. by manufacturers of plastic materials which conform to a B.S. specification and to manufacturers of plastic products, e.g. mouldings, provided that such articles comply with the relevant B.S. specifications. The use of the certification mark in relation to mouldings is intended to give the purchaser an assurance that the product conforms to a recognized standard in respect of both material and workmanship. A series of specifications for specific articles will be issued in due course, but it will clearly be impracticable to prepare individual specifications for every type of article that can be made in plastics. A general definition of "technical mouldings" laying down the minimum requirements to be complied with by a moulding to qualify for the use of the B.S.I. Certification Mark has therefore been drawn up and has been published as B.S. 1253 : 1945. For the purpose of this standard a technical moulding is defined as a moulding made to the specification of a manufacturer who uses the moulding as an assembly part.

This specification can be obtained from the British Standards Institution, Publications Department, 28, Victoria Street, London, S.W.1. Price 1s.

BEETLE CEMENTS.—The war story of these materials has now been published by British Industrial Plastics, Ltd., in a very attractive booklet entitled "The War Record of Beetle Cements for Wood." For the public the news of Beetle cements broke when the story of the Mosquito was told. We might add that it was exciting for the plastics industry itself, although the older glues were already being superseded in many industries. The news of the production of gap-filling cements was of tremendous importance in itself, for it cut completely across the theories.

The booklet is well illustrated with typical examples of structures built with Beetle cements. It has been put together by Cecil D. Notley Advertising, Ltd.

"THE OVERSEAS ENGINEER"

Following the recent death of Mr. Roland H. Briggs, M.B.E., the Founder and Editor of "The Overseas Engineer," this journal has now been taken over by Temple Press Limited.

Notables of Bakelite, Ltd. Left to right: Mr. H. V. Potter, managing director; Mr. G. J. Taylor, sales manager, Thermosetting Division; Mr. G. Dring, director and research and development manager; Mr. A. Lloyd, works manager, Thermosetting Division; Mr. G. W. Hodds, chief purchasing manager, and Mr. F. J. Robinson, director and general works manager.

BAKELITE, LTD., DINNER.—A dinner was given to members of the Distribution Department at headquarters and to the Sales Staff of Bakelite, Ltd., at the Waldorf Hotel, on Monday, February 11, during which the opportunity was taken to welcome back to the company those members who had been serving with H.M. Forces. Sixty guests were present and the General Distribution Manager, Mr. C. C. Last, took the chair. The company's headquarters executives, including the managing director, were present, and Mr. H. V. Potter, in a brief address, outlined the post-war policy of the company. A similar function was held at the Tyseley Works of Bakelite, Ltd., on Friday, February 8.

ERINOID, LTD.—We are informed by Erinoid, Ltd., Lightpill Mills, Stroud, Glos., that they have opened new offices at 3, Coleshill Street, Birmingham, 4 (telephone, Central 1886), which will be the headquarters of their Midland Division.

This will be under the control of Mr. Eric King, who for many years has been their Midlands Technical Representative and is well known throughout the industry, while he will also have the assistance of Mr. R. Tuck, who has recently returned to the company after five years in the Services. We understand, too, that Mr. G. T. Armstrong has been released from the R.A.F. after six years' absence from the company, and has joined the staff of the London office on Technical Sales.

MR. HERBERT KING (late Lieut. R.N.V.R.), of Crystalate, Ltd., Plastic Moulders, Golden Green, near Tonbridge, Kent, has resumed his position as one of the representatives of the company in London and will be re-establishing his contacts shortly, after nearly six years' service.

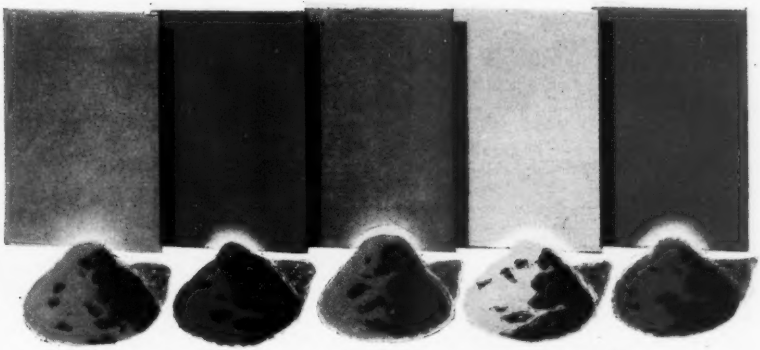
MR. A. E. JUDGE, A.M.I.E.E., has joined the Technical Sales Staff of The New Insulation Company Limited, Gloucester, and will be in charge of its London Office.

Society Meetings

The Society of Chemical Industry (Plastics Group) announce the following meetings: On March 20, Dr. J. Hofton, of British Industrial Plastics, Ltd., will give a lecture on "Aminoplastic Adhesives" at Gas Industry House, 1, Grosvenor Place, London, S.W.1, at 6.30 p.m. On March 22, Mr. N. J. L. Megson will give a lecture on "Production and Application of Plastics in Wartime," at the Physics Lecture Theatre, University College, Cardiff, at 7 p.m.

Index to "Plastics"

The Index to Vol. IX of this journal is now ready and may be obtained from this office, price 7d. post free.



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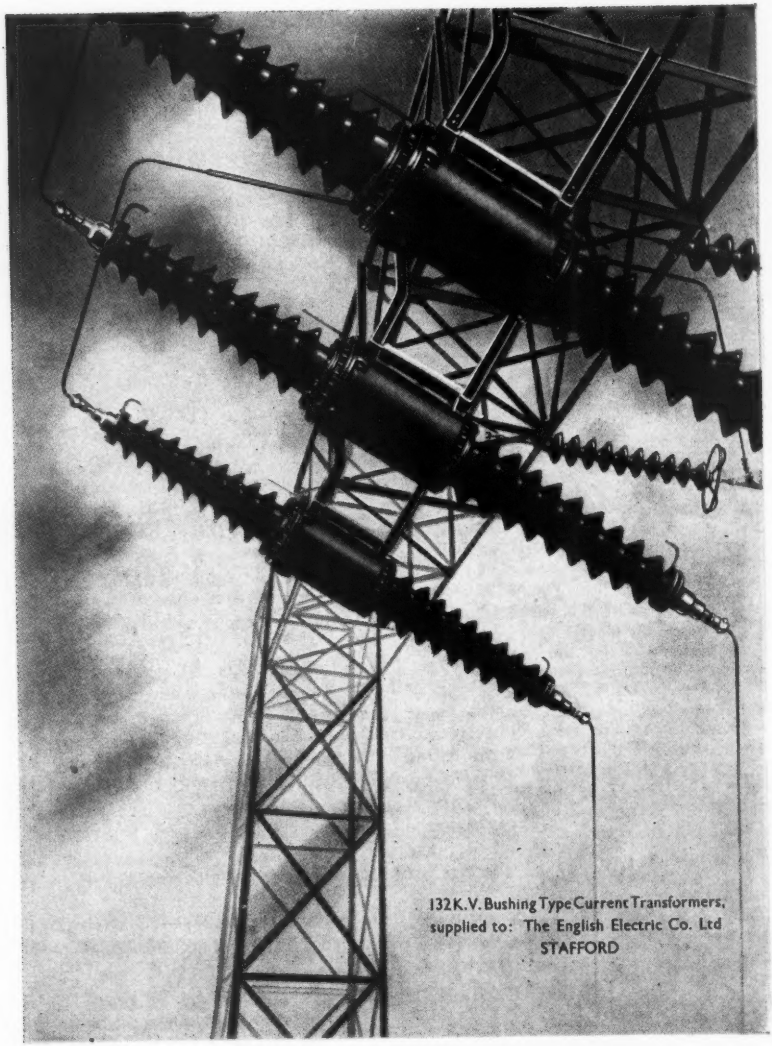

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PATENT REVIEW

B.P. 573,016. Application date: 25.6.42. Convention date (U.S.A.): 28.6.41. Accepted: 2.11.45.

Improvements in or relating to the polymerization of Styrene or of its polymerizable derivatives. To: Bakelite, Ltd.

Process for polymerizing styrene or its derivatives by heating the monomer in the presence of an organic compound (e.g., oxalic acid) and boric acid as catalyst.

B.P. 573,021. Application date: 24.7.42. Accepted: 2.11.45.

Improvements in and relating to Methods of and Apparatus for treating articles under Pressure with High Frequency Electric Heating. B. Jablonsky.

Refers to high frequency heating tools and jigs for laminated materials.

B.P. 573,024. Application date: 19.8.42. Convention date (U.S.A.): 7.11.41. Accepted: 2.11.45.

Manufacture of Synthetic Rubber-like Materials. To: E. I. de Pont de Nemours and Co.

Relates to rubber-like products obtained from chloroprene and isoprene, which have improved working properties in the plastic state and also have superior freeze resistance in the cured state. It claims a process for the production of a plastic material obtained by polymerizing a mixture of about 50-95 per cent. 2-chloro-1, 3-butadiene, and 5-50 per cent. 2-methyl-1.3-butadiene, coagulating the polymer and subsequently plasticizing it by working it in the presence of thiuram.

B.P. 573,049. Application date: 14.8.42. Accepted: 5.11.45.

Improvements in and relating to Rubber Derivatives and Synthetic Resinous Condensation Products, including Rubber or Rubber Derivatives. F. J. W. Popham. To: British Rubber Producers Research Association.

Method for preparing rubber derivatives by dispersing rubber or reclaimed rubber in phenol or cresol containing a metallic soap (e.g., cobalt naphtenate) as catalyst and subsequent oxidation. The solution containing the oxidized rubber may then be reacted with a condensing agent (e.g., formaldehyde) until the resin precipitates. This resin may be separated by distillation of the solvent. It can be used as an adhesive, for impregnation or as a moulding powder.

B.P. 573,050. Application date: 14.8.42. Accepted: 5.11.45.

Improvements in and relating to the Preparation of Rubber Derivatives. F. J. W. Popham. To: British Rubber Producers Research Association.

This is an addition to B.P. 462,627, but in this case reclaimed rubber is oxidized by dispersing it over a wide surface. Oxidation is improved by the presence of a metallic catalyst. Powdered wood pulp or alpha-cellulose is employed to enlarge the surface, and milling of the reclaimed rubber is carried out prior to the oxidation process.

B.P. 573,054. Application date: 14.9.42. Accepted: 5.11.45.

Improvements in or relating to the reclaiming of Vulcanized Rubber containing Cellulosic Material. P. H. Amphlett, A. J. Hughes and D. F. Twiss. To: Dunlop Rubber Co., Ltd.

B.P. 573,055. Application date: 18.9.42. Convention date (U.S.A.): 18.9.41. Accepted: 5.11.45.

Improvements in or relating to the Interpolymerization of Acrylonitrile. To: Imperial Chemical Industries, Ltd.

B.P. 573,058. Application date: 1.10.42. Accepted: 5.11.45.

Improvements in or relating to the Production of Fabrics from Alginic Materials. J. B. Speakman and N. H. Chamberlain. To: Cefoil, Ltd.

Method of producing alkali-resistant fabrics from alginic materials by using an alkali-soluble type (calcium alginate), and subsequently converting the material into an alkali-resistant type. Conversion process: (1) Removal of calcium by treatment with N/10 HC1; (2) Treatment with basic Cr-Acetate, Be-acetate or formaldehyde, to form alkali-resistant cross linkages of the molecules.

B.P. 573,062. Application date: 20.10.43. Convention date (U.S.A.): 20.10.42. Accepted: 5.11.45.

Emulsion Polymerization of Organic Materials. To: Imperial Chemical Industries, Ltd.

Relates to copolymers of natural rubber with vinyl compounds.

B.P. 573,081. Application date: 12.10.42. Convention date (U.S.A.): 13.10.41. Accepted: 6.11.45.

Process for Improving the Tensile Strength and other Properties of Synthetic Linear Polyamide Articles. du Pont de Nemours.

Method of improving the properties of synthetic linear polyamides by heating these polyamides above 120 degrees C. but below their melting point as determined in an inert atmosphere, whilst tension is applied.

B.P. 573,086. Application date: 20.10.43. Convention date (U.S.A.): 20.10.42. Accepted: 6.11.45.

Production of Copolymers of Isobutylene by Emulsion Polymerization. E. I. du Pont de Nemours.

B.P. 573,083. Application date: 17.10.42. Accepted: 6.11.45.

Improvements in or relating to the Manufacture of Synthetic Resins. E. J. Lush. To: Peter Lunt and Co., Ltd.

Process for making resinous products by reacting an aluminium alcoholate (e.g., aluminium butyl alcoholate) and an aluminium phenate in the presence of aluminium powder at temperatures between 100-150 degrees C. The alcohol-phenate mixture may be dissolved in a solvent inert to SO_2 (e.g., carbon tetrachloride) and SO_2 passed through until the solution becomes red in colour and clear.

B.P. 573,101. Application date: 18.11.43. Accepted: 6.11.45.

Improvements in or relating to Presses for the Vulcanization of Tyres. T. Norcross. To: Dunlop Rubber Co.

Mechanical design of a tyre-moulding press, where top and bottom moulds are interlinked and closed by means of cam mechanism. The relative position of the top mould is adjustable by means of screws, and the approach of the two half-moulds can be controlled by the design of the cam.

B.P. 573,109. Application date: 31.7.42. Convention date (U.S.A.): 16.10.41. Accepted: 7.11.45.

Improvements in or relating to Catalytic Isomerization of Paraffin Hydrocarbons and Catalysts therefor. Standard Oil Development Co.

Method of preparation of an aluminium chloride catalyst for use in the isomerization of normal and branched chain paraffins.

B.P. 573,112. Application date: 30.10.42. Accepted: 7.11.45.

Improvements in and relating to the Manufacture of Rubber-like Materials. G. Shaffer. To: Kenilworth Manufacturing Co.

Method for making rubber-like materials by heat polymerization of shellac or other lac resins, esterified with a monohydric diphatic alcohol. Polymerization is carried out at temperatures between 15-200 degrees C., preferably in the presence of a catalyst such as sulphuric acid, benzoyl-peroxide, etc.

B.P. 573,114. Application date: 28.10.42. Accepted: 7.11.45.

Improvements in and relating to resinous Condensation Products and Moulding Compositions produced therefrom. F. J. W. Popham. To: British Rubber Producers Research Association.

Method of preparing synthetic resins from phenol, formaldehyde and oxidized rubber in the presence of a basic catalyst.

B.P. 573,115. Application date: 29.4.42. Accepted 7.11.45.

Improvements in or relating to Moulding and Thermoplastic Compositions and a Process for the Manufacture of Products therefrom. S. A. Leader.

Concerns compositions suitable for plastic surgery, comprising polymeric or monomeric methyl methacrylate and salol, the latter being present in amounts from 5-120 per cent., preferably between 50-100 per cent. Other acrylates and vinyl resins in proportions not exceeding 10 per cent. by weight of the methyl-methacrylate may be added. (See also B.P. 550,252.)

B.P. 573,148. Application date: 19.11.42. Accepted: 8.11.45.

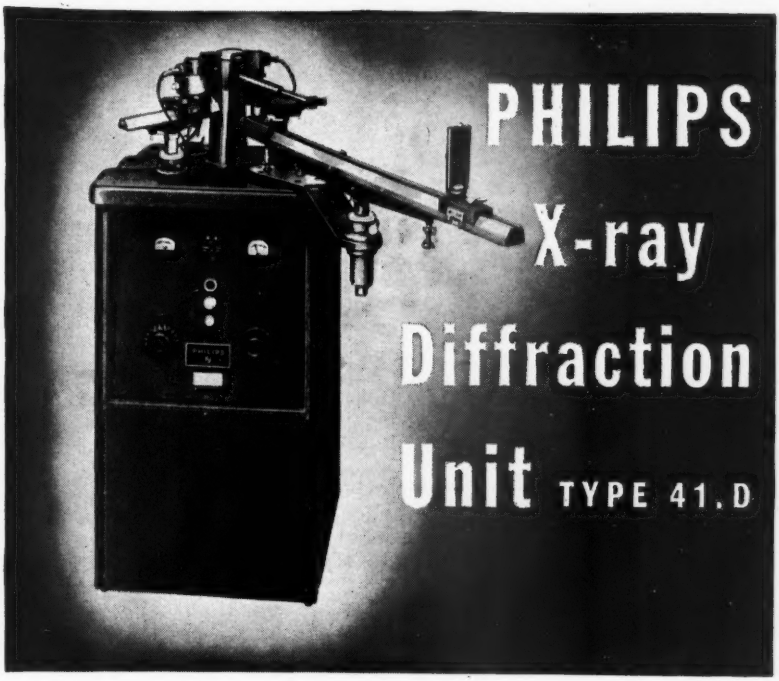
Improvements in or relating to the Production of Alginic Yarns. J. B. Speakman and N. H. Chamberlain. To: Cefoil, Ltd.

Method for the production of yarn from alginic acid or calcium alginate, where the filament unwound from the cake is washed in a continuous process, and subsequently dried continously in a drying chamber prior to being reeled for use. It is claimed that shrinkage can be controlled in this manner, and that the finished product is free from defects created when washing and drying are attempted in hank form.

B.P. 573,236. Application date: 1.5.44. Accepted: 12.11.45.

Improvements in or relating to the Production of Sheet Wrapping Materials. W. Berry and F. W. Pritchard. To: British Cellophane, Ltd.

Concerns a sheet wrapping material pro-



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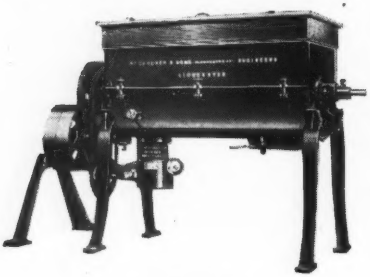

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viding complete protection from ultraviolet rays, thus preventing rancidification of the goods packed therein. These sheets (of regenerated cellulose) contain salts of bis [(p-amino-benzoyl) −4 : 41 diamino stilbene-2 : 2¹-disulphonic acid] and glycerine as softening agent.

B.P. 573,270. Application date: 7.1.42. Accepted: 14.11.45.

Production of Polymeric Materials. R. G. R. Bacon, S. G. Jarrett and L. B. Morgan. To: Imperial Chemical Industries, Ltd.

Process for manufacturing polymeric materials by polymerizing acrylic acid, alpha-chloracrylic acid, methacrylic acid or their saponifiable derivatives with or without other compounds of a polymerizable olifinic nature, in an aqueous medium in the presence of persulphuric acid or a water-soluble persulphate and sodium hydro-sulphite.

B.P. 573,306. Application date: 3.7.41. Accepted: 15.11.45.

Improvements in the Manufacture of Cellular Polymerized Ethylene. G. M. Hamilton. To: Callendars Cable and Constr. Co.

Process for making polyethylene in cellular form by subjecting the solid material to a pressure between 100-300 lb./sq. in. exerted by CO_2 at a temperature approx. 30 degrees C. below the softening point of the polythene, subsequently releasing the external pressure, thus causing expansion of the gas. This is followed by cooling.

B.P. 573,308. Application date: 23.10.41. Accepted: 15.11.45.

Improvements in and relating to the Preparation, Treatment and Application of Resins. L. A. Jordan and J. K. Aiken.

Improved or modified resins of the polysulphide type for incorporation into varnishes and coating compositions.

B.P. 573,333. Application date: 1.4.42. Accepted: 16.11.45.

Improvements in and relating to the Preparation, Treatment and Application of Resins. L. A. Jordan and J. K. Aiken.

Similar to B.P. 573,308.

B.P. 573,339. Application date: 1.7.42. Accepted: 16.11.45.

Pulverulent Preparations of Rubber-like Condensation Products. H. Taylor. To: I.C.I., Ltd.

Relates to the production of rubber-like condensation products from beta-beta-dichlorodiethyl ether and alkali metal polysulphides alone or in admixture with minor proportions of natural and synthetic resins.

B.P. 573,366. Application date: 4.6.41. Accepted: 19.11.45.

Polymerization of Vinyl Chloride. R. G. R. Bacon, L. B. Morgan. To: I.C.I., Ltd.

Process for polymerizing vinyl chloride by itself or together with other compounds of olefinic nature, in an aqueous medium in the presence of a water soluble persulphate and sodium hydrosulphite or sodium bisulphite.

B.P. 573,369. Application date: 4.11.41. Accepted: 19.11.45.

Production of Polymeric Materials. R. G. R. Bacon, J. R. Lewis, L. B. Morgan. To: I.C.I., Ltd.

Relates to the production of polymers from unsymmetrical dichloroethylene by polymerization in an aqueous medium alone or together with other polymerizable compounds containing a $> C = CH$ group in the presence of a water soluble persulphate (or persulphuric acid) and sodium hydro-sulphite.

B.P. 573,375. Application date: 12.4.43. Accepted: 19.11.45.

Improvements in or relating to the Manufacture of viscous protein solutions for the Production of Artificial Filaments and Filaments derived therefrom. R. H. Kendal Thomson, S. R. Swift. To: I.C.I., Ltd.

Relates to the manufacture of viscous aqueous alkaline solutions of peanut globulin which can be used in the production of filaments.

B.P. 573,403. Application date: 27.5.43. Convention date (U.S.A.): 14.11.42. Accepted: 20.11.45.

Improvements in methods and apparatus for spinning artificial filaments, films and the like. G. T. Detwiler, M. P. Kulp, S. A. Moss, Jnr., and H. D. Merion. To: American Viscose Corporation.

Method for extruding filaments through dies into a water bath. Special care is taken to prevent any turbulence in the bath. This purpose is achieved by providing the die with a protecting sleeve which extends into the bath and does not obstruct the passage of liquid to the filament as it leaves the emulsion die.

B.P. 573,430. Application date: 27.2.42. Accepted: 21.11.45.

Phenol Formaldehyde Resins. W. Charlton and J. B. Harrison. To: I.C.I., Ltd.

Relates particularly to the manufacture of oil soluble resins from o-Cresol, by reacting o-Cresol in admixture with minor proportions of monohydric phenols (e.g., p-tertiary butyl phenol, p-cyclohexyl phenol, p-cresol) with an equimolecular proportion of formaldehyde in the presence of an alkaline catalyst (caustic soda). These resins can be blended with drying oils and be used for varnishes.

B.P. 573,437. Application date: 30.10.42. Accepted: 21.11.45.

Improvements in and relating to Synthetic Resins. H. C. Bryson. To: Scott Bader and Co., Ltd.

Synthetic resins of the phenol-formaldehyde type modified by the presence of not more than 1/20 of a polyvinylal type resin (Alvar, Formvar or Butvar) used for coatings.

B.P. 573,456. Application date: 12.5.44. Convention date (U.S.A.): 20.5.43. Accepted: 21.11.45.

Production of Vinyl Cyanide. To: E. I. du Pont de Nemours and Co.

B.P. 573,473. Application date: 15.4.43. Convention date (U.S.A.): 22.5.42. Accepted: 22.11.45.

Improvements in or relating to Plastic sheets convertible to Dichroic Polarizers and Image Carriers. To: International Polaroid Corp.

Method for the production of polarizing film used for the stereoscopic images, consists of producing a thin sheet of polyvinyl alcohol. The molecules of the sheet surface are oriented by stretching or other mechanical processes. The sheets are bonded together with the directions of surface orientations at right angles to one another for use in the production of dichroic stereoscopic images. Materials usable are polyvinyl alcohol and its derivatives.

B.P. 573,474. Application date: 15.4.43. Convention date (U.S.A.): 22.5.42. Accepted: 22.11.45.

Improvements in or relating to Plastic Sheets of Films convertible to Dichroic Polarizers and Image Carriers. International Polaroid Corp.

Method of producing plastic films of non-hydrophilic nature and making composite sheets from these for use as dichroic polarizers. One layer is made of polyvinyl alcohol, while the other layer, which is bonded to the first layer, may consist of cellulose acetate or cellulose acetate butyrate. Materials also named for the second layer are: cellulose nitrate, ethyl cellulose derivatives, acetals, ketals and organic esters of polyvinyl alcohol, polymerized esters of acrylic and metacrylic acid and their derivatives.

B.P. 573,482. Application date: 2.6.43. Convention date (U.S.A.): 3.6.42. Accepted: 22.11.45.

Improvements in or relating to the production of derivatives of Linear Polyamides. To: E. I. Du Pont de Nemours and Co.

B.P. 573,518. Application date: 15.10.43. Convention date (U.S.A.): 27.2.43. Accepted: 23.11.45.

A method of, and apparatus for, bonding materials electrically. To: Radio Corporation of America.

High frequency seam welder with positively driven rollers. Bottom roller large diameter and earthed, top roller small diameter and live. H.F. energy, 10 watts to 150 watts. Frequencies: 10 to 100 mc/s. Provision for water-cooling of rollers. Adjustable spring pressure for top roller. Various types of continuous and intermittent seams. Means for feeding plastic cement between rollers.

B.P. 573,529. Application date: 9.6.41. Accepted: 26.11.45.

Synthetic Rubber-like Materials. B. J. Habgood, R. Hill and L. B. Morgan. To: I.C.I., Ltd.

Process for manufacturing rubber-like materials by inter-polymerization of a mixture of butadiene-1:3 (or a methyl or dimethyl derivative thereof) with less than an equal part (by weight) of an anilide or methyl substituted anilide of acrylic acid or methacrylic acid, in aqueous emulsion in the presence of catalysts.

B.P. 573,530. Application date: 4.7.41. Accepted: 26.11.45.

Improvements in or relating to the manufacture and application of Synthetic Rubber-like Materials. H. Gudgeon, E. Isaacs and W. McGillivray to Imperial Chemical Industries, Ltd.

Process for making rubber-like materials by interpolymerization of butadiene-1:3 or 2-chlorobutadiene-1:3 (or their methyl- or ethyl derivatives) with a coniugated diene having chloro and cyano-substituents.

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B.P. 573,536. Application date: 7.4.43. Convention date (U.S.A.): 24.6.42. Accepted: 26.11.45.

Method of preparing Chlorinated Rubber. W. H. Stevenson. To: Hercules Powder Co.

Process for the production of chlorinated rubber of extremely high viscosity (at least 7,000 centipoise) in order to yield highly flexible and tough sheets. Chlorination under controlled time and temperature conditions.

B.P. 573,561. Application date: 3.11.41. Accepted: 27.11.45.

Improvements in or relating to the Manufacture of Vinyl Chloride. H. M. Stanley and G. Minkoff. To: the Distillers Co., Ltd.

Process for the manufacture of vinyl chloride from acetylene and hydrogen chloride in vapour form in the presence of mercury chloride as catalyst.

B.P. 573,567. Application date: 19.3.42. Accepted: 27.11.45.

Method of Polymerization. A. M. Borders, W. D. Wolfe, H. J. Osteshof and C. W. Walton.

Method for the production of rubber-like materials by copolymerization of butadiene and a vinyl compound (acrylonitrile, styrene, etc.) in the presence of hydrogen peroxide (as catalyst) and an aliphatic aldehyde such as acetaldehyde and a water soluble cyanide.

B.P. 573,594. Application date: 13.10.42. Accepted: 28.11.45.

Improvements in or relating to the manufacture of Vinyl Chloride. H. M. Stanley, G. Minkoff and J. E. Youell. To: the Distillers Co., Ltd.

Process for the manufacture of vinyl chloride by reacting acetylene with hydrogen chloride. The latter is obtained as a by-product in the dehydrochlorination of chlorinated organic compounds (e.g., ethylene dichloride) and is freed from contaminating saturated chlorinated organic compounds by washing so that not more than 8-15 per cent. is left.

B.P. 573,596. Application date: 10.11.42. Convention date (U.S.A.): 13.6.42. Accepted: 26.11.45.

Method of producing alpha-Halo-Acrylates. Wingfoot Corporation.

B.P. 573,597. Application date: 10.11.42. Accepted: 28.11.45.

Production of Tetrahydrofurfuryl alpha-Chloroacrylate. Wingfoot Corporation.

B.P. 573,622. Application date: 21.1.42. Accepted: 29.11.45.

Improvements in or relating to the Manufacture of Synthetic Resins. Distillers Co.

Process for the manufacture of a resin by reacting a phenolic compound and an aldehyde (containing a reactive methylene group) in the presence of an alkaline catalyst and not more than 10 per cent of an aromatic amine.

B.P. 573,626. Application date: 26.11.42. Accepted: 29.11.45.

Improvements in or relating to Synthetic Resins. J. D. Morgan, B. Frenkel. To: British Resin Products, Ltd.

Relates to the production of oil soluble condensation products of cresols or their homologues with aldehydes.

B.P. 573,631. Application date: 1.1.43. Convention date (U.S.A.): 15.12.41. Accepted: 29.11.45.

Manufacture of Butadiene. W. Szukiewicz.

B.P. 573,670. Application date: 29.9.43. Accepted: 30.11.45.

Production of Vinyl Chloride. W. A. Lazier, G. M. Whitman. To: E. I. Du Pont de Nemours and Co.

Process for the production of vinyl chloride by passing a mixture of acetylene and hydrochloric acid (in gaseous form) over mercurous chloride as catalyst, at temperatures between 100 and 250 degrees C.

B.P. 573,723. Application date: 28.2.41. Accepted: 4.12.45.

Improvements in or relating to the manufacture of polymerizable unsaturated acids. J. J. P. Staudinger, K. H. W. Tuerck and E. H. Brittain. To: the Distillers Co., Ltd.

Relates to the manufacture of polymerizable unsaturated acids such as acrylic, methacrylic or chloracrylic acid from the corresponding aldehydes by oxidation with molecular alcohol.

B.P. 573,779. Application date: 6.12.43 Convention date (U.S.A.): 8.12.42. Accepted: 5.12.45.

Improvements in the production of ornamental and other effects on organic Ester of Cellulose Materials.

B.P. 573,805. Application date: 16.12.43. Accepted: 6.12.45.

Improvements relating to the Production of Resins. T. Scott and G. Baddeley. To: Refiners, Ltd.

Refers to the recovery of polystyrene, polycoumarone or polyindene from naphtha.

LETTERS TO THE EDITOR

Microscopic Examination of Plastics

Sir,—We have followed with interest the work of Mr. J. H. Wredden entitled "The Microscopic Examination of Plastic Materials," and appreciate the time and energy that must have been devoted to the carrying out of his examination in such detail. Nevertheless, as manufacturers of Plastic materials for a number of years, we cannot accept without comment Part V on Insulating Sleevings, because of some of the inaccuracies contained therein.

The types of sleeving that Mr. Wredden has examined are mainly those which demand has created, and not for the suggested reason that manufacturers are unable to produce anything of better quality. Whatever the deficiencies of the sleevings may be, they have fulfilled the requirements of designers who are not easily persuaded to use better quality materials at higher prices, when types of inferior quality will fulfil their requirements satisfactorily.

Mr. Wredden's statement "that materials are combined by methods that more or less ignore the fundamental principles underlying their combination," credits manufacturers with little technical ability, simply because he has not examined a completely impregnated braid, yet he himself has failed to mention one important aspect of impregnation—viz., the difference between the chain length of the impregnating medium and that of the material to be impregnated, which is important in using synthetic materials.

In his examination of Group 4 materials he has "presumed" the use of a highly viscous solution of polyvinyl acetate or chloride copolymer, which has been rapidly applied as a single layer. In practice several coats of quite low-viscosity solutions are used, and the fact that no lines of separate application appear between layers is due to the welding of each successive coat to the previous one by virtue of the common solvent used in the lacquer formation. This does not happen with successive coats of oil-based varnishes, because the oxidized coat is not affected by the varnish base, or the diluents employed with it.

The assumed use of cuprammonium viscose having a water absorption of only one per cent. is entirely new to us and very doubtful, since we are not aware of any type of viscose having a water absorption of much less than 10-12 per cent., which makes the value of 10.64 per cent. for this Type 4 sleeving not unexpected.

The use of P.V.C. as an insulant coupled with an internal silk lining is a unique construction, and the silk is used solely to provide a high-temperature gradient between the conductor wire and the insulant to overcome soldering difficulties and heat drift generally. This silk lining, however, virtually acts as a good conductor when the sleeving is subjected to voltage test under wet conditions. This condition imposes a full voltage stress throughout the full length of the plastic insulating film, a condition which does not obtain in other forms of insulating sleeving where point contact only exists between the conductor and the insulant wall on test.

The fact that this type of sleeving, presumably our Permanoid "VS" grade, satisfactorily complies with the new and stringent BS/RCS Specification, represents, in view of these abnormally severe testing conditions, a very considerable technical achievement.

It is to be regretted that the author did not complete his investigation by correlating electrical characteristics with water absorption. The results would have been more revealing since from our experience Type 4 material is very much superior to varnished types of the same class, both before and after subjection to humid and tropical exposure conditions.

As manufacturers of the insulating sleevings falling within the author's Type 4, we would ask you kindly to publish these comments in order to prevent an entirely misleading conception of the design and performance of a product which, in our view, represents the only outstanding advancement in the manufacture of impregnated braids over a period of 120 years, since the days when Faraday first used a braid coated with varnish. Permanoid "VS" not only provides good electrical insulation, but is also designed to meet many other modern requirements such as flexibility at low temperatures, freedom from ageing at high temperatures, freedom from mould growth and termite action, imperviousness to oils and petrol, high surface insulation and extensive colour range. Many of these modern demands have not been considered at all by the author, yet modern electrical requirements make them essential. Without these ancilliary properties we can all be certain that the development of electronic

equipment during the war would have been greatly impeded. Permanoid "VS" contributed, for example, largely to the successful development of Radar, not so much because of its electrical characteristics but because of such useful ancillary properties as mentioned above.

L. W. TOWNSEND,

For and on behalf of Associated Technical Manufacturers, Ltd.

Mr. Wredden's Reply

Dear Sir,—Thank you for your letter of the 21st inst., together with enclosed copy of Mr. Townsend's letter.

I should like to thank Mr. Townsend for his opening remarks and for the detailed criticism in which he has indulged. His notes on the points raised are so interesting that I should like to take this opportunity of replying to them in some detail.

I should first like to correct the impression of any intention to suggest that the manufacturers were unable to produce a material of better quality, but rather to point out that as a result of subjecting components to examination under the microscope, one is led to conclude that the manufacturing processes are of a very involved nature, as indicated by the six closely inter-related points raised in the first article (November, 1945), which, it would appear, are by no means the sum total of similar factors.

In the same article I have given it as my opinion that in view of the difficulties involved, the manufacturers are to be congratulated on the results produced to-day, but surely this does not imply that efforts to improve these sleevings should cease because the user does not want a better material. Rather should these efforts be redoubled in order that the user may have better materials to draw upon; after all, unless the user knows what the manufacturer is capable of producing, he is not in a position to ask for anything better, except by vague suggestions.

With regard to the latter part of this second paragraph relating to prices. Whereas I am personally only interested in the scientific aspect of the subject, I have made references to prices and here again, it seems to me that prices are largely dependent on demand, as it would be logical to assume that to produce an ideal structure, such as I have suggested, would cost more, at least at first.

This cost would fluctuate with the demand, but with its rise would lead to further improvements in plant and methods, resulting in a lowering of the cost. After all, the development of the plastic industry is a classic example of the operation of this law.

With regard to the question of the requirements of designers, I would suggest that no good designer of electrical apparatus would sacrifice quality at the expense of slight extra cost.

Continuing with the third paragraph, here again it was not intended as a condemnation of the technical ability of manufacturers, but rather to emphasize the complex nature of the task undertaken, inasmuch as the sleevings do not appear to have been made with a knowledge of all the operative functions governing the combination of the materials. A misunderstanding appears to have arisen as a result of my use of the word "principles" when "functions" (meaning the six factors previously referred to) would have conveyed the meaning more clearly.

Mr. Townsend goes on to say that I have not examined a completely impregnated braid. In reply to this I would state that throughout the three articles in question I have stressed the necessity of aiming at the hypothetical ideal of complete impregnation, by which is meant the embedding of every fibre composing the yarn, in a solid continuous matrix, to the entire exclusion of pockets of air or other foreign bodies, and after repeatedly stressing this ideal, demonstrated its existence in the form of varnished natural silk (illustrated in Fig. 46, December, 1945). I further went on to show the advantages of this by giving breakdown and puncture voltage figures.

I am, however, grateful to your correspondent for raising the point of the part played by chain length. This is important and is, of course, another operative function to be added to the list. Its greatest effect would appear to be with regard to viscosity and as such would have the inter-related effects on the impregnating properties of the varnish, but at the same time I would like to suggest that the question of surface tension is rather more important when it comes to trying to reach the ideal structure. These two characteristics were examined briefly in the first article.

When discussing the operative functions mentioned, I pointed out that they were not all those involved. As a matter of fact, I have since been informed by a reader that I left out the factor of "time of immersion," and no doubt there are many other factors still unknown. However, as I did not feel justified in embarking on a lengthy and

involved discussion of these factors, I chose what appeared to me to be the most important and I think a detailed examination of the effect of viscosity would naturally include the effect of chain length.

In the fourth paragraph of Mr. Townsend's letter, my conclusion that the resin coating of the sleeving under discussion was applied in one thick coating appears to be wrong, and I am pleased that Mr. Townsend has seen fit to point out the mistake. However, being a representative of the user, we know very little about the secrets of varnished sleeving manufacture, though it does raise an interesting point. I note that Mr. Townsend states: "In practice several coats of quite low viscosity are used." This may be so, but there would appear to be something wrong with the surface tension; this is indicated by the poor depth of impregnation, as shown in Fig. 50 (January issue). As I have tried to show, the initial surface tension would seem to be of paramount importance and this in itself is complex since the surface tensions relative to so many materials have to be taken into account. Thus if the surface tension is high, the difficulties accompanying the process of impregnation increase and the result shown would be produced, whether the resin was applied by a series of thin coats or not, although the chances of producing this result with a single application would be much greater than with multiple coats.

With regard to the fifth paragraph of Mr. Townsend's letter concerning the moisture absorption of cuprammonium viscose which I quoted as 1 per cent., I would like to say that this figure is a mistake on my part, for which I take full responsibility. The actual reabsorption of cuprammonium is 10 to 11 per cent., which, as Mr. Townsend states, "makes the value of 10.64 per cent. for this type 4 sleeving not unexpected." This does not mean a great deal of modification of my views on the subject of complete impregnation, because if this yarn were completely protected according to the ideal concept, then the moisture absorption of the sleeving as a whole would be expected to be no more than that of the material composing the matrix. On the other hand, it seems to lay greater emphasis on the necessity for 100 per cent. impregnation.

This question of moisture absorption of cellulose is interesting, as it appears that when water is absorbed from the desiccated condition it shows a tendency to go into loose combination with the hydroxyl groups on the cellulose chain, in which circumstance Mr. Townsend will no doubt appreciate the difficulties involved in eliminating it. Stoving is doubtless the best method. Therefore, if the cellulose is to be used in its most efficient state (as an insulator), it must be thoroughly dry and completely impregnated. It all depends whether one looks upon the braid as a supporting medium for the resin or varnish, or whether one considers it as an integral part of the insulator, functioning as such. It seems to me that the best way of regarding the function of the braid is to look upon it as a component of the insulator, in the nature of a filler, much as one would the paper in a phenolic laminate, in which case it serves the dual function of strengthening medium and insulant, assuming that there is 100 per cent. impregnation. In this way the braid would be used at its maximum efficiency.

Mr. Townsend continues with a reference to the use of a sleeving consisting of a P.V.C. tube, having an internal lining of silk braid and mentions the reason for this construction as being due to the necessity for overcoming the failings of P.V.C. At high temperatures this is, of course, quite logical, but it raises an interesting point on which I should, if I may, ask a question. This is regarding the statement that when the silk lining is wet it becomes conducting and in doing so evens out the stress in the P.V.C. This condition might be perfectly satisfactory in certain circumstances, but I am not at all sure as to its behaviour at high frequencies. As far as I can see, the losses due to the wet silk under these conditions would be high and it might even be possible to generate sufficient heat in this manner as to cause the water to be converted into steam, irrespective of the effect on the P.V.C.

In view of the increasing use of the higher frequencies, this point would appear to be of some importance, hence my repeated stressing of the necessity for an homogeneous product.

Apart from this, one must not overlook the effects of ionization, for, when it is appreciated that oxygen is quoted by Moelwyn-Hughes to possess an ionizing voltage of 13.56, further comment on the importance of this aspect is unnecessary. I do not, however, fully appreciate Mr. Townsend raising the point of the behaviour of the silk lining when wet, as this is by no means the normal working condition. When it is dry, the condition, of course, reverts to that of a large number of point

contacts (microscopically speaking) with relatively large volumes of air present in the interstices of the braid.

No doubt the sleeving quoted by Mr. Townsend does stand up to the stringent specification mentioned. I suggest that the success obtained in this direction is an incentive to still further development and research.

I note that Mr. Townsend regrets that I did not take the subject further and correlate electrical characteristics with water absorption. I can appreciate this remark as nobody would be more pleased than myself to see such information published. I would like to remind your correspondent that the subject of the articles was the microscopic examination of the materials in question and all the conclusions and hypotheses put forward were the result of this examination; as it is, I have been guilty of straying from the subject and I think that an analysis such as that suggested would more appropriately come from Mr. Townsend himself. I need not emphasize that such information would be welcomed by all, as the published data on sleevings in general is sketchy.

J. H. WREDDEN.

PLASTICS FROM PETROLEUM

(Contd. from p. 155).

relation to the plastics industry in this country. We are not an oil-producing country to any great extent and most of the essential raw material will have to be imported. Will it be worth while? In answer we may quote from Dr. F. Kind's address to the Society of Chemical Industry ["Chemistry and Industry," **20,** 183, (1944)]:—

"I hear frequently the argument about whether it is wise to use petroleum at all as a raw material for the chemical industry in view of the fact that it has to be imported, whereas coal is readily available. I think this is an extremely fallacious argument, because, if an industry based on an imported raw material is considered unsound, then our cotton industry, the greater part of the wool industry, and practically the whole of the metal industry are in the same boat—only with the important difference that, whilst a ton of crude petroleum yields about 98 per cent. by weight of useful products, the wastage in the other industries based on imported raw material is considerably higher."

Book Review

Raw Materials from the Sea

The sea contains in solution vast quantities of inorganic salts and organic compounds available for the use of man. Relatively little has been taken from this storehouse, and Dr. E. F. Armstrong, F.R.S., who was recognized by every chemist in the country as one of its greatest scientific leaders, and Mr. L. M. Miall, B.A., have compiled a book under the title "Raw Materials from the Sea" in the hope that man may one day turn more seriously to this inexhaustible supply for our raw materials.

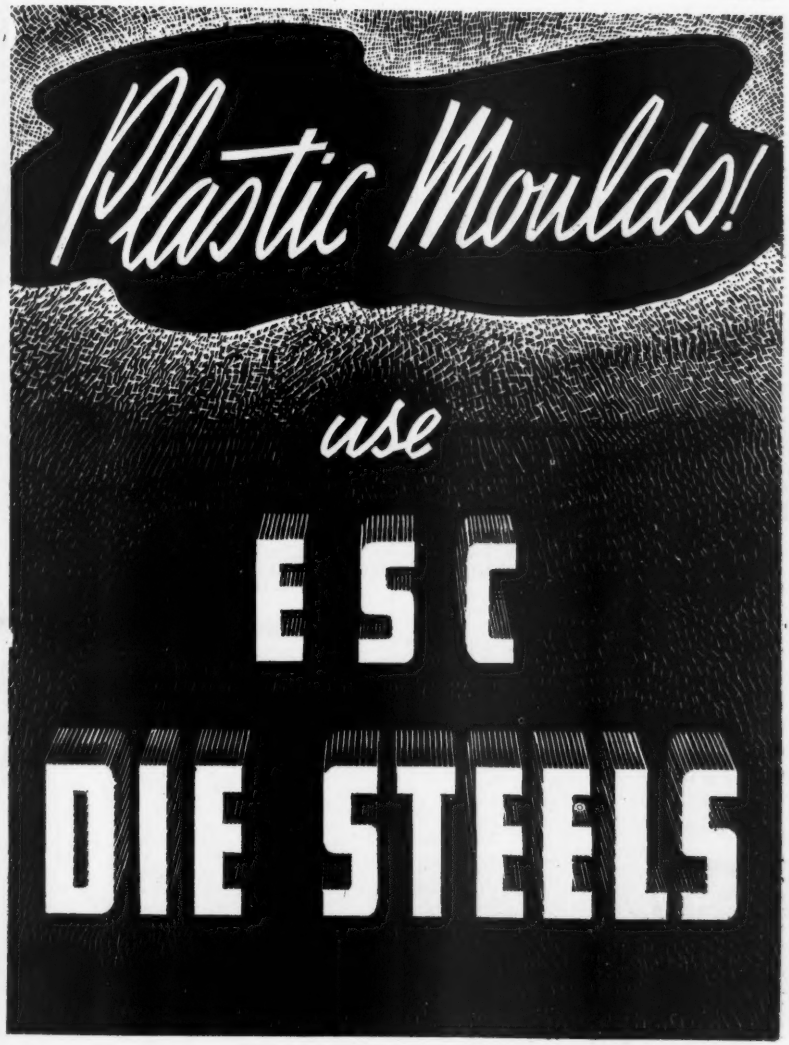
Common salt has been obtained since time immemorial. Potassium and iodine have been extracted from the Dead Sea for some 20 years. Magnesium and bromine, too, are now manufactured in large quantities in America and elsewhere.

The story of how this may be accomplished is of absorbing interest, and the authors have contrived to give the reader new and surprising facts, showing what the sea contains, and what has been accomplished in winning back from the sea substances which for countless ages the rivers have washed to the sea.

The authors suggest that the sea has a volume of the order of 300 million cubic miles, and proceed to discuss in simple language the available data leading to an estimate of the quantities of the various chemical substances and metallic elements, ranging from gold to magnesium, which are available to those who are prepared to install suitable extraction plant and apparatus.

The biochemistry of the ocean forms an important section of the book, which should appeal to non-technical members of the general public who are interested in matters scientific, as well as to chemical engineers and students of science in colleges and universities, and all concerned politically, industrially, or financially with the world's supplies of raw materials.

The book is published by Constructive Publications Ltd., Leicester, at 15s. net.



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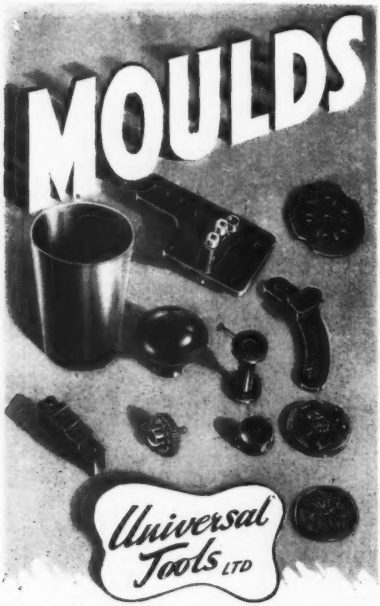

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